J. Indian Chem. Soc., Vol. LXI, No. 7. Pp. 565—654 ISSN 0019-4522

July 1984

CODEN : JICSAH LXI, (7) (1984), 565—654

JOURNAL

OF THE

INDIAN CHEMICAL SOCIETY

Published by The Indian Chemical Society

92, Acharya Prafulla Chandra Road,

Calcutta-700 009

INDIAN CHEMICAL SOCIETY

92, ACHARYA PRAFULLA CHANDRA ROAD
CALCUTTA-700 009

Price of Publications :

1. Catalogue of Physico-Chemical Standard Substances ;
   Reprinted from Pure and Applied Chemistry, Vol. 29(4), 601-16, (1972)
   (With the kind permission of the International Union of Pure and Applied Chemistry)

   Price : Rs. 4 (Inland, inclusive of postage)
   Rs. 8 (Foreign, inclusive of postage by Surface Mail).

2. Acharya Prafulla Chandra Ray : Life and Achievements
   by Prof. N. R. Dhar :

   Price : Rs. 5 (Inland, inclusive of postage)
   Rs. 10 (Foreign, inclusive of postage by Surface Mail).

3. Reflections on Chemical Education by Prof. N. R. Dhar :

   Price : Rs. 12.50 (Inland, inclusive of postage)
   Rs. 25.00 (Foreign, inclusive of postage by Surface Mail).

4. History of Chemistry in Ancient & Medieval India
   Edited by Prof. P. Ray :

   Price : Rs. 30.00 (Inland, inclusive of postage)
   Rs. 75.00 (Foreign, inclusive of postage by Surface Mail).

5. Abstracts of XX-ICCC (held at Calcutta in December, 1979)

   Price : Inland : Rs. 325.00 (Inclusive of Regd. postage by Surface Mail)
   Foreign : Rs. 425.00 or U. S. $ 50.00 (Inclusive of Regd. Air Mail postage).

6. Calcutta (A Tourist Guide Book)

   Price : Inland : Rs. 15.00 (Inclusive of postage)
   Foreign : Rs. 25.00 (Inclusive of postage by Surface Mail).

Annual Subscription (inclusive of postage) for the Journal of the Indian Chemical Society (for Non-Fellows) for 1984 :

Rs. 400.00 (Inland) ; U.S. $ 125.00 (Foreign) ; Air Postage Extra. (May be paid in equivalent Indian Rupee).

Back issues of the Journal of the Indian Chemical Society and Indian Journal of Applied Chemistry (upto 1972 ; discontinued from January, 1973) may be available, for which separate enquiries are to be made for availability and rates.

I. Kar
Executive Secretary

Journal of the Indian Chemical Society

VOLUME LXI NUMBER 7 JULY 1984

CONTENTS

CONTENTS

CONTENTS

CONTENTS

AUTHOR INDEX

Journal of the Indian Chemical Society

VOLUME LXI NUMBER 8 AUGUST 1984

CONTENTS

CONTENTS

CONTENTS

CONTENTS

AUTHOR INDEX

Journal of the Indian Chemical Society

VOLUME LXI NUMBER 9 SEPTEMBER 1984

CONTENTS

CONTENTS

CONTENTS

CONTENTS

AUTHOR INDEX

Journal of the Indian Chemical Society

VOLUME LXI NUMBER 10 OCTOBER 1984

CONTENTS

CONTENTS

CONTENTS

CONTENTS

AUTHOR INDEX

ISSN 0019-4522

J. Indian Chem. Soc., Vol. LXI, No. 11, 12. Pp. 923-1124

November, December 1984

CODEN : JICSAH LXI, (11, 12) (1984), 923-1124

JOURNAL OF THE INDIAN CHEMICAL SOCIETY

PROFESSOR MAHENDRA KUMAR ROUT 60TH BIRTHDAY COMMEMORATION ISSUE

Published by The Indian Chemical Society
92, Acharya Prafulla Chandra Road,
Calcutta-700 009



Professor Mahendra Kumar Rout
Ph.D., D.Sc.
(Born : 4th January, 1924)

Professor of Chemistry, Ravenshaw College, Cuttack (1961-1968) ; Principal, G. M. College (1968-1970) ; D.P.I., Orissa (May-September, 1980) ; Vice-Chancellor, Utkal University (1980-1983 Sept.) ; At present, Chairman, Orissa State Prevention and Control of Pollution Board and Honorary President, Regional Recruitment Board, State Bank of India. Recipient, Cooper Memorial Medal two times, 1964 and 1966 ; Member of Scientific-Delegations to U.S.A. (1956) and U.S.S.R. (1969) ; Member of the delegation of six educational administrators to U.S.A. (1977) ; An outstanding teacher, research worker and educational administrator.

FOREWORD

This issue of the Journal of The Indian Chemical Society is dedicated to Professor M. K. Rout, at present, Chairman, Orissa State Prevention and Control of Pollution Board and Honorary President, Regional Recruitment Board, State Bank of India.

Professor Rout, a member of the Council of the Indian Chemical Society for several years, is one of the most eminent Chemists of the country. The areas of his research work spread over diverse fields—drugs, dyes, oils, alkaloids, quantum-mechanical interpretation of structure-spectra correlation, theoretical studies involving correlation equations, and polymerisation.

At present he is deeply involved in researches on Industrial and Environmental Pollution and his book "Control of Pollution in Industries in Orissa" released on June 5, 1984, the World Environment Day, is being highly acclaimed as an excellent reference material for pollution control measures.

An outstanding teacher, he used to take classes right from the first year to sixth year even when he was the Principal of Ravenshaw College and post-graduate classes even as the Vice-Chancellor of Utkal University.

About 40 students have got Ph.D. under his guidance. He is still engaged in active research and is guiding a number of research students.

As the Vice-Chancellor of Utkal University, he had the unique distinction of converting a deficit of Rs. 1.5 crores into a fixed deposit of Rs. 50 lakhs. During his tenure as the Vice-Chancellor, the University Intermediate and the Degree results were being published consistently in time.

On the occasion of his sixtieth birthday, Prof. Rout was felicitated by his students, collegues and eminent citizens of Orissa at a function arranged by Prof. Rout 60th Birthday Celebration Committee, on the 17th February, 1984.

A souvenir booklet published on this occasion gives his biographical sketch, a brief resume of his scientific contributions, a list of his publications, the names of his Ph.D. students and also messages from eminent professors, citizens from both inside and outside the State.

This issue, which is a tribute to Dr. Rout's contribution in the field of chemical research, chemical education and educational administration, contains only invited original articles alongwith a few review articles. We are grateful to the distinguished Scientists who have graciously responded to our invitation.

It is our proud privilege to convey, on behalf of the Celebration Committee, our gratitude to the Council of the Indian Chemical Society for accepting our proposal for the publication of this commemorative volume. We are particularly grateful to Professor S. K. Talapatra, Honorary Secretary and Dr. S. K. Roy, Executive Editor for their co-operation. We owe thanks to Dr. D. M. Puri and Dr. K. Lal for their assistance in editing this issue.

H. K. Pujari
(Kurukshetra University, Kurukshetra)
Honorary Editor, and Vice-President,

G. B. Behera
(Sambalpur University, Sambalpur)
Honorary Editor, and Secretary,

Prof M. K. Rout 60th Birthday Celebration Committee,

Journal of the Indian Chemical Society

VOLUME LXI NUMBERS 11, 12 NOVEMBER, DECEMBER 1984

CONTENTS

CONTENTS

CONTENTS

CONTENTS

AUTHOR INDEX

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 565-567

Copper(II), Nickel(II), Cobalt(II), Manganese(II), Zinc(II) and Iron(III) Complexes of γ-(3-carboxy-4-hydroxy-benzoyl)butanoic Acid

M. N. PATEL and M. R. CHAUDHARI

Chemistry Department, Sardar Patel University, Vallabh Vidyanagar-388 120

Manuscript received 2 April 1983, revised 13 March 1984, accepted 17 June 1984

Cu^{II}, Ni^{II}, Co^{II}, Mn^{II}, Zn^{II} and Fe^{III} complexes of γ-(3-carboxy-4-hydroxybenzoyl)butanoic acid have been synthesised and characterised on the basis of analytical, spectral, thermal and magnetic measurements. Various ligand (10 D_q) and nephelauxetic parameters (B and β) have been evaluated for octahedral Ni^{II} and Co^{II} complexes. Tetrahedral structures are suggested for Mn^{II} and Zn^{II} while octahedral and square planar structures are suggested for Fe^{III} and Cu^{II} complexes. The infrared spectra reveal that (i) the aromatic corboxylic group is deprotonated while the phenolic group hydrogen remains intact and, (ii) metal ion is bonded to both the carboxylic oxygen and phenolic oxygen.

SALICYLATE complexes of many metals including those of transition metals have been reported by a number of workers[1,2], but most of these studies have been carried out in solution. Some workers have studied salicylato-complexes in the solid state but conflicting results have been reported[3-5]. However, there is no mention in the literature of any reaction between γ-(3-carboxy-4-hydroxy-benzoyl)butanoic acid, γ-(CHB)BA and transition metals. The present paper describes the preparation and characterisation of transition metal complexes of γ-(CHB)BA. In the formation of metal complexes of various derivatives of salicylic acid, the phenolic group dissociates and which plays an important part in the complex formation[6]. In the present investigation we found that the carboxylic proton dissociates while the phenolic group remains intact.

Experimental

Preparation of γ-(3-carboxy-4-hydroxybenzoyl) butanoic acid: Polyphosphoric acid (50 g) was added to a mixture of salicylic acid (69 g, 0.05 mol) and glutaric acid (9.9 g, 0.075 mol) and then heated at 130° for 6 h. The solid obtained was added to ice-cold water, filtered and washed with hot water. It was purified by dissolving in NaOH solution (10%) and reprecipitated with ice-cold HCl (10%) as a brown coloured compound (78.3%), m.p. 160°. It is soluble in alcohol.

Preparation of complexes: A general procedure was adopted to synthesise the complexes. Cu^{II}, Ni^{II}, Co^{II}, Mn^{II}, Zn^{II} and Fe^{III} chloride (0.01 mol, 20 ml) was mixed with ligand in absolute alcohol (0.02 mol, 50 ml; 0.03 mol, 75 ml for Fe^{III} complex). The resulting precipitates obtained by addition of sodium acetate were washed with hot water and ethanol and dried in vacuum desiccator.

Elemental analyses and physical measurements: Carbon and hydrogen analyses were performed by Coleman carbon hydrogen analyser. The metal contents of the complexes were determined according to standard procedures[7]. The analytical data are given in Table 1. Room temperature magnetic susceptibilities were measured by Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. Magnetic moments were corrected for the temperature-independent paramagnetism. Ir spectra (KBr) were recorded in UR-10 spectrophotometer. Diffuse reflectance spectra in the solid state were obtained from a Beckman DU spectrophotometer using MgO as reference. TG data were obtained from an assembly capable of producing temperature upto 800° with a heating rate of 10° min^{-1}.

Results and Discussion

The analytical data of the complexes support the proposed formulations. All the complexes are stable under normal conditions and insoluble in common organic solvents. The percentage loss in weight (found, calcd.) on heating above 150° for Ni^{II} (6.0, 6.01%) and Co^{II} (5.51, 6.01%) complexes indicate the presence of two coordinated water molecules[8]. The formation of respective metal oxides occurs at 600-700°. The decomposition temperatures are given in Table 1.

The most important ir bands of diagnostic value and their tentative assignments for the ligand and its complexes are listed in Table 2. In the carboxylato-complexes symmetrical (ν_s) and asymmetrical (ν_a) stretching modes of COO group

TABLE 1—ANALYTICAL AND MAGNETIC MOMENT DATA OF COMPLEXES

Complex	Decomp. temp. °C	μ_{eff} B.M.	Analysis % : Found/(Calcd.) C	H	M
γ(CHB)BA	300		57.68 (57.14)	5.36 (4.79)	
Cu[γ(CHB)BA]$_2$	250	1.9	50.56 (50.93)	4.10 (3.91)	11.55 (11.22)
Ni[γ(CHB)BA.H$_2$O]$_2$	250	3.1	48.20 (48.27)	4.41 (4.38)	10.07 (9.83)
Co[γ(CHB)BA.H$_2$O]$_2$	200	5.1	48.31 (48.25)	4.22 (4.38)	10.21 (9.86)
Mn[γ(CHB)BA]$_2$	275	6.2	51.80 (51.71)	4.00 (3.97)	9.50 (9.27)
Fe[γ(CHB)BA]$_3$	250	5.9	53.85 (53.41)	4.31 (4.10)	7.38 (6.89)
Zn[γ(CHB)BA]$_2$	200	diamagnetic	51.11 (50.76)	4.21 (3.90)	11.93 (11.51)

TABLE 2—SPECTRAL CHARACTERISTICS OF COMPLEXES

Complex	Frequency cm^{-1}	Transition	COO ν_{as}	COO ν_s	M-O	
γ(CHB)BA			1680	1620		
Cu[γ(CHB)BA]$_2$	20000 15384	$^2B_{1g} \rightarrow {}^2E_g$ $^2B_{1g} \rightarrow {}^2B_{2g}$	1600	1440	530	
Ni[γ(CHB)BA.H$_2$O]$_2$	25000 20000 11000	$^3A_{2g} \rightarrow {}^3T_{1g}$ (P) $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) $^3A_{2g} \rightarrow {}^3T_{2g}$ (F)	1610	1460	530	$10D_q = 11000$ $B = 800$ $\beta = 0.76$
Co[γ(CHB)BA.H$_2$O]$_2$	20833 8474	$^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P) $^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$	1600	1460	550	$10D_q = 9660$ $B = 903$ $\beta = 0.93$
Mn[γ(CHB)BA]$_2$	22220 21052 19230	$^6A_1 \rightarrow {}^4E_1$ $^4A_1$ (G) $^6A_1 \rightarrow {}^4T_2$ (G) $^6A_1 \rightarrow {}^4T_1$ (G)	1600	1450	560	
Fe[γ(CHB)BA]$_3$	20000	$^6A_{1g} \rightarrow {}^4T_{1g}$ (F)	1600	1450	540	
Zn[γ(CHB)BA]$_2$	—		1600	1450	500	

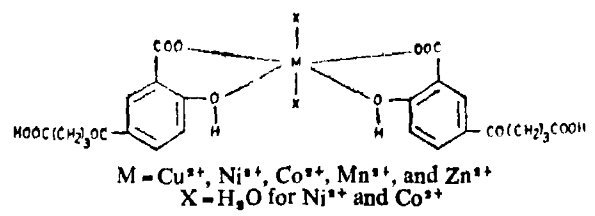
are of much importance since their positions and separation can help in determining the type of bonding. It has been accepted[9] that the covalent character of M-O increases with an increase in $\Delta\nu$ COO. In present investigation aromatic COO stretching frequencies in γ-(CHB)BA have been found to be sensitive to coordination to the metal. In all the complexes, the ν_s COO and ν_{as} COO modes are observed at 1450 and 1600 cm^{-1}, respectively. The $\Delta\nu$ COO value is about 150 cm^{-1} which indicates the covalent character of M-O bond. In ligand ν_{O-O} of aromatic COOH is observed at 1670 cm^{-1} and aliphatic COOH is observed at 1700 cm^{-1}. The 1700 cm^{-1} band does not shift on complexation which indicates aliphatic COOH is free in complexes. A strong band at 1220 cm^{-1} in ligand is assigned to ν_{C-O} of phenolic group which shifts to 1150 cm^{-1} on complexation[10]. The broad band observed at ~ 3300 cm^{-1} can be assigned to the absorption of the coordinated OH group[11]. All the complexes show weak band at 580-600 cm^{-1} due to M-O bond[12]. The ir spectra suggest that the coordinated carboxylic group acts as monodentate.

The copper(II) complex under study has a magnetic moment value of 1.9 B.M. The magnetic moment of the nickel complex 3.1 B.M. is in the expected range of divalent nickel in an octahedral field[13]. The Co^{II} complex exhibits magnetic moment 5.1 B.M. indicating it to be high spin with three unpaired electrons and having octahedral stereochemistry[14]. 6.2 B.M. value for the Mn^{II} complex is as expected for five unpaired electrons[15]. The iron(III) complex has 5.4 B.M. value which is lower than expected for high spin complex. The

low value of magnetic moment can be interpreted in terms of antiferromagnetic behaviour[16].

The diffuse reflectance spectra (Table 2) of Cu^{II} complex shows two bands and together with magnetic moment value suggest a square planar geometry[17]. In the case of Ni^{II} complex the transitions are characteristic of octahedral stereochemistry[18]. The ratio ν_2/ν_1 (1 : 80) lies in the range required for Ni^{II} octahedral complexes[19]. In high spin Co^{II} complexes the experimentally observed spin-allowed transitions in increasing order of energy are ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and are denoted as ν_1, ν_2 and ν_3, respectively. The reflectance spectra of Co^{II} complex shows two bonds which are assigned to octahedral stereochemistry[20]. Using $10D_q$ (9660 cm^{-1}) and B (903 cm^{-1}), ν_2 was calculated. The ratio ν_2 (calcd.)/ν_1 (found) is 2.14 as required for octahedral Co^{II} complexes. The value of B for the free gaseous ion, 972 cm^{-1}, is used to calculate the value for nephelauxetic ratio, β (0.93). In Mn^{II} complexes the intensity of the electronic transitions from the ground state (${}^6S$) to the states of four-fold multiplicity are very weak[21]. Since Mn^{II} has a d^5 configuration the same type of energy level diagram applies whether the metal ion is surrounded by tetrahedral or octahedral environment. Here, the Mn^{II} complex exhibits bands which are assigned to tetrahedral stereochemistry[22]. The Fe^{III} complex shows broad peak at 20000 cm^{-1} which may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (F) transition for octahedral stereochemistry[23]. The Zn^{II} complex is diamagnetic and may have tetrahedral structure.

In view of these observations the following structures may be assigned to the complexes.



M = Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Zn^{2+}
X = H_2O for Ni^{2+} and Co^{2+}

Acknowledgement

The authors express their sincere thanks to Prof. S. R. Patel, Head of the Department of Chemistry for providing laboratory facilities and encouragement. One of the authors (M.R.C.) is grateful to the U.G.C., New Delhi for financial assistance.

References

1. J. P. TANDON and R. C. MEHROTRA, *J. Indian Chem. Soc.*, 1961, **38**, 169.
2. P. K. KHADILKAR and S. N. KAKKAR, *Indian J. Chem., Sect. A*, 1976, **14**, 621.
3. B. I. SKANAVI, M. S. GRIGOREVA and F. B. GLIKINA, *Zh. Neorg. Khim.*, 1960, 283.
4. V. K. CHERNAYA and S. Y. SHNAIDERENMANI, *Tekhnal*, 1965, 33, 42.
5. H. C. MISHRA and R. R. JHA, *J. Indian Chem. Soc.*, 1980, **57**, 769.
6. M. C. CHATTOPADHYAYA and R. S. SINGH, *Indian J. Chem.*, 1972, **10**, 850.
7. A. I. VOGEL, "Quantitative Inorganic Analysis", E.L.B.S./Longmans, London, 1969.
8. N. S. BHAVE and R. B. KHARAT, *J. Indian Chem. Soc.*, 1980, **57**, 385.
9. M. R. UDUPA and G. K. RAMACHANDRA, *J. Indian Chem. Soc.*, 1981, **58**, 430.
10. P. C. SRIVASTAVA and B. K. BANERJEE, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1771.
11. M. R. MAHMOUD and M. T. EL-HATY, *J. Inorg. Nucl. Chem.*, 1980, **42**, 349.
12. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, 1970.
13. A. K. SRIVASTAVA, V. B. RANA and MADAN MOHAN, *J. Inorg. Nucl. Chem.*, 1974, **36**, 2118.
14. B. N. FIGGIS and J. LEWIS, *Prog. Inorg. Chem.*, 1964, **6**, 37.
15. M. MOHAN and B. D. PARAMHANS, *Indian J. Chem., Sect. A*, 1980, **19**, 759.
16. A. SYAMAL and K. S. KALE, *Indian J. Chem., Sect. A*, 1982, **21**, 439.
17. B. N. FIGGIS, "Introduction to Ligand Fields", Interscience, New York, 1967, p. 316.
18. L. SACCONI, "Transition Metal Chemistry", Marcel Dekker, New York, 1968, Vol. 4, p. 211.
19. D. K. RASTOGI and K. C. SHARMA, *J. Inorg. Nucl. Chem.*, 1974, **36**, 2219.
20. J. LEWIS and R. S. WILKINS, "Modern Coordination Chemistry", New York, 1960, p. 290.
21. S. A. COTTON, *Coord. Chem. Rev.*, 1972, **8**, 185.
22. C. FURLANI and A. FURLANI, *J. Inorg. Nucl. Chem.*, 1961, **19**, 51.
23. P. C. SRIVASTAVA, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3613.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 568-570

Mixed Ligand Complexes of Cobalt(II), Copper(II) and Zinc(II) with Acetoacetanilide and Some Other Nitrogen Donor Ligands

BIPIN B. MAHAPATRA and DEBENDRA PANDA

Department of Chemistry, G. M. College, Sambalpur-768 004

Manuscript received 22 July 1983, revised 21 March 1984, accepted 17 June 1984

Mixed ligand complexes of cobalt(II), copper(II) and zinc(II) with acetoacetanilide and some other nitrogen donor ligands of compositions [MX(acacN)B], [MX(acacN)-$(H_2O)_2$], [MX(acacN)B_2H_2O] and [MX(acacN)B_2], where M = Co^{II}, Cu^{II}, Zn^{II}; X = Cl^-, Br^-, NO_3^-, ClO_4^-; acacN = acetoacetanilide anion; B = pyridine, γ-picoline, quinoline, have been prepared. The compounds have been characterised on the basis of analytical, conductance, magnetic susceptibility, ir and electronic spectral data. The thermal decompositions of a few cobalt(II) and copper(II) complexes were studied by DTG and DTA techniques.

SYNTHESIS of metal complexes having unusual coordination numbers through a process of mixed ligation has evoked a lot of interest in recent years. Several mixed ligand pentacoordinated complexes of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) have been reported[1-5] using oxygen, nitrogen and sulphur donor ligands. It was therefore thought worthwhile to study the reactions of Co^{II}, Cu^{II} and Zn^{II} with acetoacetanilide in 1 : 1 stoichiometric proportions in the presence of nitrogen donor ligands. The present paper reports some tetra-, penta-, and hexacoordinated mixed ligand complexes of Co^{II}, Cu^{II} and Zn^{II} ions.

Experimental

All the chemicals were of AnalaR grade.

[Co(NO_3) (acacN)(H_2O)$_3$] and [Cu(NO_3)(acacN) (H_2O)$_2$]: The compounds of this type were prepared by reacting the ethanolic solution of cobalt(II) nitrate (2.9 g) and copper(II) nitrate (1.9 g) and acetoacetanilide (1.7 g) in hot ethanol separately followed by dropwise addition of ammonia with constant shaking.

[MX(acacN) B_2H_2O]: Metal salts, acetoacetanilide and the nitrogen donor ligands (1 : 1 : 2 mol) in ethanolic medium were reacted under reflux. The resulting solutions were then neutralised by adding conc. ammonia dropwise with shaking.

[MX(acacN)B]: These were prepared by reacting metal salts, acetoacetanilide and nitrogen donor ligands in ethanolic medium (1 : 1 : 1 mol). The reaction mixture was refluxed for 1 h over a water-bath. Conc. ammonia was then added slowly dropwise to the slightly warm solution when the metal complexes separated out.

[Co(NO_3) (acacN)Q_2] and [Co(NO_3) (acacN) (γ-Pic)$_2$]: These compounds were obtained by reacting the ethanolic solutions of cobalt(II) nitrate (2.9 g), acetoacetanilide (1.7 g) and quinoline (2.5 ml) and γ-picoline (1.9 ml) separately and refluxing the contents for nearly 1 h. Conc. ammonia was then added dropwise to the moderately hot solution when the compounds separated out.

The compounds thus isolated were filtered, washed with ethanol several times followed by ether and dried *in vacuo*.

Metal and nitrogen contents in the complexes were estimated by the usual methods. Conductance was measured in 10^{-3} *M* acetone solution of the complexes. Magnetic susceptibility measurements were made on the solid samples by the Gouy method. The ir spectra (KBr) were recorded on Perkin-Elmer 398 spectrophotometer. The electronic spectra were recorded in 10^{-3} *M* acetone solution, using Hilger and Watt Uvispeck spectrophotometer. Thermogravimetric analyses were carried out by the Hungarian Optical Works, Hungary, in the ambient temperature of the furnace with a heating rate of $10°min^{-1}$. Analysis, molar conductance, magnetic susceptibility and ir data are given in Table 1.

Results and Discussion

Based upon the analytical and conductance data, the complexes have the following compositions: [M(NO_3) (acacN) (H_2O)$_3$], M=Co^{II}, Cu^{II}; [MX(acacN)B_2 H_2O], M=Co^{II}, Cu^{II} and X= Cl^-, NO_3^-; [Mx(acacN)B], M=Co^{II}, Zn^{II} and X=

TABLE 1

Sl. no.	Compd.	Colour	M. p.	μ_{eff} B.M.	Analysis % : Found (Calcd.) M	N	ν_{C-O} / $\nu_{C=O}$	ν_{M-O} / ν_{M-N}
1.	CoCl LQ	Blue	235	4.6	14.75 (14.58)	7.00 (6.85)	1100 / 1625	450 / 520
2.	$CoClL(\gamma\text{-pic})_2H_2O$	Violet	237	5.0	15.79 (15.65)	11.23 (11.08)	1105 / 1620	445 / 510
3.	$CoClL(py_2)H_2O$	Violet	200	5.0	13.22 (13.18)	9.41 (9.27)	1100 / 1620	440 / 515
4.	$Co(NO_3)L(H_2O)_2$	Pink	>280	5.1	16.80 (16.69)	8.00 (7.88)	1105 / 1615	445 / 510
5.	$Co(NO_3)L\,Q_2$	Leafy green	>280	4.8	10.63 (10.50)	10.09 (9.85)	1100 / 1620	450 / 515
6.	$Co(NO_3)L(\gamma\text{-pic})_2$	Leafy green	>280	4.85	12.21 (12.10)	11.59 (11.46)	1100 / 1625	445 / 520
7.	$Co(ClO_4)L(\gamma\text{-pic})_2$	Brown	210	5.0	9.62 (9.51)	9.13 (9.05)	1100 / 1620	440 / 515
8.	$CuClL(\gamma\text{-pic})_2H_2O$	Blue	172	1.78	11.07 (10.90)	8.76 (8.68)	1105 / 1620	445 / 510
9.	$CuClL\,Q_2H_2O$	Blue	200	1.77	11.43 (11.35)	7.62 (7.58)	1100 / 1625	440 / 515
10.	$Cu(NO_3)L(H_2O)_2$	Green	>280	1.79	17.74 (17.60)	7.89 (7.78)	1105 / 1620	450 / 510
11.	$Cu(NO_3)LQ_2H_2O$	Blue	215	1.78	10.91 (10.78)	9.70 (9.56)	1100 / 1620	445 / 520
12.	$Cu(ClO_4)L(\gamma\text{-pic})_2$	Chocolate	140	1.78	12.00 (11.89)	8.00 (7.86)	1095 / 1615	445 / 520
13.	$ZnClL(\gamma\text{-pic})$	White	222	–	17.61 (17.56)	7.58 (7.47)	1100 / 1620	440 / 510
14.	ZnClL Q	Brown	220	–	16.50 (16.38)	6.91 (6.76)	1105 / 1625	440 / 515
15.	$ZnBrL(\gamma\text{-pic})$	White	140	–	15.70 (15.59)	6.76 (6.67)	1100 / 1615	450 / 510
16.	ZnBrL(py)	White	205	–	16.25 (16.18)	7.00 (6.88)	1100 / 1625	445 / 520

L = acetoacetanilide anion, γ-pic = γ-picoline, py = pyridine, Q = quinoline.

Cl^-, Br^- ; $[MX(acacN)B_2]$, $M=Co^{II}$ and $X=ClO_4^-$; $[MX(acacN)B_2]$, $M=Co^{II}$, Cu^{II} and $X=ClO_4^-$, NO_3^- ; acacN=acetoacetanilide anion, B= pyridine, γ-picoline, quinoline.

The ir active bands at 1630 (C=O), 1590 (C=C) and 1150 cm^{-1} (C–O) in acetoacetanilide moiety appear at ~ 1620, 1580 and 1100 cm^{-1}, respectively in the metal complexes. Hence it may be concluded that the ligand (acacNH) is bonded to the metal ions through both the amidic and enolic oxygen atoms. Further evidence of bonding of oxygen atom is provided by the appearance[6] of metal-oxygen band at ~ 450 cm^{-1} in the far ir spectra of the complexes. In case of cobalt(II) and copper(II) perchlorate complexes, two sharp bands are observed at 985 and 1100 cm^{-1} indicative[7] of the coordinated perchlorate group in conformity with conductance data. Strong absorption bands at ~ 1370 and 1215 cm^{-1} suggest unidentate coordination[8,9] of the nitrato complexes. This is also supported by the conductance data. Most of the absorption bands due to the heterocyclic bases get shifted in the mixed ligand complexes indicating their bonding to the metal ions. The sharp band observed at 3300 cm^{-1} (NH) in the free ligand and in the metal complexes indicates the non-coordination of the amidic nitrogen atom of acetoacetanilide molecule to the metal ions. In case of some cobalt(II) and copper(II) complexes, the presence of coordinated water is ascertained by the observation[10,11] of a broad double hump at ~ 3450 cm^{-1} followed by the appearance of a sharp peak at ~ 840 cm^{-1}. The appearance of the bands at ~ 520 cm^{-1} in the far ir spectra of mixed ligand complexes indicates the bonding of metal ions with different heterocyclic nitrogen atoms thereby confirming their presence in the complexes. Metal-halogen stretching frequencies however, fall beyond the range of the instrument used.

In the electronic spectra of cobalt(II) complexes (Sl. nos. 2,3,4 and 7 of Table 1), the absorption bands at ~ 8,450(11), 18,500(24) and 20,00(32) cm^{-1} have been attributed to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $\rightarrow {}^4A_{2g}(F)$ and $\rightarrow {}^4T_{1g}(P)$ transitions, respectively in conformity with an octahedral configuration[12,13]. This is supported by the high magnetic moment values as well[7]. In the case of cobalt(II) complexes (Sl. nos. 5 and 6) three bands are observed at ~ 19,600 (ν_4), 15,260 (ν_3) and 11,400 (ν_2) cm^{-1} in

conformity with the earlier observation[14,15] for pentacoordinated Co^{II} complexes. In the electronic spectrum of quinoline adduct of chlorocomplex (Sl. no. 1), two bands are observed at 15,300 (1400) and 8,500 (210) cm^{-1} assignable to $^4A_2 \rightarrow {}^4T_{1g}(P)$ and $^4A_2 \rightarrow {}^4T_{1g}(F)$ transitions, respectively. The high extinction coefficient value of $^4A_2 \rightarrow {}^4T_{1g}(P)$ and low μ_{eff} value (4.6 B.M.) support a tetrahedral configuration for the complex. All the copper(II) complexes except the perchlorate complex show a broad band in the 13,750–14,300 cm^{-1} region due to $^2E_g \rightarrow {}^2T_{2g}$ transition[12] indicating a distorted octahedral stereochemistry of the complexes. A single broad band is noticed for the perchlorato complex at 15,400 cm^{-1} in conformity with the spectral band for the penta-coordinated copper(II) complexes reported[16].

The thermogravimetric study of four representative compounds have been reported. The cobalt complex [Co(acacN)Cl (γ-pic)$_2$ H_2O] starts losing its mass gradually with the rise of temperature and between 80-160°, as observed from the TGA graph, loses the water molecule with a weight loss of 3.87%. Then again it loses one molecule of γ-picoline as evident from the sharp endothermic peak at 250° on the DTA curve with a weight loss of 23.87% against the observed value 23.26%. With the rise of temperature it loses again the second molecule of γ-picoline at 340° with a loss of 43.8%. Then the compound starts losing its weight and at 600°, shown by the sharp endothermic peak, loses 1/3rd. of the acetoacetanilide molecule with a loss of 56.7% against the theoretical value 57.5%. Again it loses 1/3rd. of acetoacetanilide at 800° as evident from the sharp exothermic peak with a loss of 69.4%. Then the compound loses rest 1/3rd. of acetoacetanilide moiety along with chlorine atom with a loss of 86.3% weight as shown by the sharp DTA exothermic peak at 960° with the formation of CoO. The complex [CoCl (acacN) (py)$_2$ H_2O] loses the water molecule and one molecule of pyridine at 190-280° with a loss of 21.7% weight as evident from two sharp endothermic peaks on DTA curve. Thereafter it loses the second molecule of pyridine at 280-360° with a loss of 39.3% (38.6% theoretical). Then the compound loses 1/3rd. of the acetoacetanilide molecule (loss 52.7%) at 360-540° and then rest 2/3rd. of the acetoacetanilide along with chlorine atom at 540-960° with the formation of CoO. The compound [CoCl(acacN)Q] loses the quinoline molecule at 245-300° shown by the sharp exothermic peak at 250° with a loss of 32.14% (32.25% theoretical). Then it loses 1/3rd. of acetoacetanilide molecule at 360° as evident from the sharp endothermic peak with a loss of 46.3%. Then it loses 1/3rd. molecule of acetoacetanilide at 660° shown by the endothermic peak with a loss of 62.4% weight (61.7% theoretical). Then the compound starts losing its weight and at 880° it loses the rest 1/3rd. of acetoacetanilide along with the chlorine atom with a loss of 82.2% (81.9% theoretical) with the formation of CoO.

The copper complex [CuCl(acacN)(γ-pic)$_2$ H_2O] loses the water molecule at 140° shown by the sharp exothermic peak on DTA curve with a loss of 3·8% weight. Then it loses one molecule of γ-picoline as evident from the small exothermic peak at 180° with a loss of 23.8% (24.5% theoretical). Thereafter it loses the second molecule of γ-picoline at 260-440° with a loss of 41.9%. Then the compound loses the acacN molecule along with chlorine atom at 440-660° with a loss of 84.9% with the formation of CuO, and subsequently a mass loss of 89.8% is observed at 660-780° with the formation of metallic copper shown by the sharp exothermic peak at 780° on the DTA curve.

Based upon analytical and conductance data four Zn^{II} complexes may be presumably four-coordinated having a tetrahedral geometry around the metal ions.

References

1. B. B. Mahapatra, B. K. Mahapatra and S. Guru, *J. Indian Chem. Soc.*, 1978, **55**, 513.
2. B. B. Mahapatra, A. Panda, S. K. Pujari and S. Guru, *J. Indian Chem. Soc.*, 1980, **57**, 372.
3. B. B. Mahapatra, S. K. Pujari and A. Chiranjeevi, *J. Indian Chem. Soc.*, 1981, **58**, 742.
4. B. B. Mahapatra, D. Panda and S. K. Pujari, *Indian J. Chem., Sect. A*, 1983, **22**, 436.
5. B. B. Mahapatra and D. Panda, *Indian J. Chem.*, in the press.
6. J. R. Ferraro, "Low Frequency Vibrations of Inorganic and Coordination Compounds", Plenum Press, New York, 1961.
7. B. J. Hathway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.
8. C. C. Addition and N. Logan, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 95.
9. N. K. Karayame, C. M. Mikuiski, L. L. Pytleuski and M. M. Labes, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3139.
10. K. Nakamoto "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley, New York, 1963.
11. I. Gamo, *Bull. Chem. Soc. Jpn.*, 1961, **34**, 760.
12. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsvier, Amsterdam, 1968.
13. J. R. Allian, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1895.
14. L. Sacconi, M. Clampoline, F. Maggic and F. P. Cavasino, *J. Am. Chem. Soc.*, 1962, **84**, 3246.
15. L. Sacconi, M. Ciampoline and G. P. Speroni, *J. Am. Chem. Soc.*, 1965, **87**, 3102.
16. R. D. Gillard and G. Wilkinson, *J. Chem. Soc. (A)*, 1963, 359.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 571-572

Study of Mixed Ligand Complexes of Nickel(II), Copper(II), Palladium(II) and Platinum(II) with Pyrrole-2-carboxaldehyde and Acetylacetone

(Miss) PREETI MEHTA and R. K. MEHTA

Chemistry Department, University of Jodhpur, Jodhpur-342 001

Manuscript received 16 August 1983, revised 21 April 1984, accepted 17 June 1984

Mixed ligand complexes of the types [MLL'], [MLL'A] and [MLE.H$_2$O] have been prepared, where M = Ni^{II}, Cu^{II}, Pd^{II}, or Pt^{II}, L = pyrrole-2-carboxaldehyde, L' = acetylacetone, A = ammonia or alkylamine, and E = ethanolamine. These complexes have been characterised by elemental analysis, magnetic, conductance and spectral studies.

IN continuation of our earlier work[1] on mixed ligand complexes, we report slightly different types of mixed ligand complexes in the present communication.

Experimental

[MLL'] type of complexes, where M=Ni^{II}, Cu^{II}, Pd^{II} or Pt^{II}, L=pyrrole-2-carboxaldehyde, and L'=acetylacetone, were prepared by adding pyrrole-2-carboxaldehyde (Fluka) and acetylacetone to the metal acetate solution in 1 : 1 : 1 ratio. The coloured solid separated was filtered and recrystallised from methanol. On reaction with excess of ammonia or alkylamines these gave [MLL'A] type complexes (A=ammonia or alkylamine) which on refluxing with ethanolamine on a water bath for 2-3 h gave [MLE.H$_2$O] type complexes (E=ethanolamine). These complexes were recrystallised from methanol.

Results and Discussion

All the mixed ligand complexes give satisfactory C, H, N and metal analysis. [MLE.H$_2$O] type complexes indicated the presence of a water molecule. Very small molar conductance values (3.2-7.2 ohm^{-1} cm^2 mol^{-1}) suggest these complexes to be non-electrolytic in nature.

The Ni^{II}, Pd^{II} and Pt^{II} complexes are found diamagnetic while Cu^{II} complexes are paramagnetic (μ_{eff}, 1.88 B.M.) at room temperature.

The electronic absorption spectra of the mixed ligand Ni^{II} complexes in methanol gave two bands at 610-620 and 535-550 nm assignable to the transitions $^1A_{1g}\rightarrow{}^1B_{1g}$ and $^1A_{1g}\rightarrow{}^1B_{2g}$, respectively. The Cu^{II} complex gave one band at 635-645 nm assignable to the transition $^2B_{1g}\rightarrow{}^2E_g$. The Pd^{II} complexes exhibited three bands in the narrow ranges at 440-450, 375-380 and 315-320 nm assigned to the transitions $^1A_{1g}\rightarrow{}^1B_{1g}$, $^1A_{1g}\rightarrow{}^1E_{1g}$ and $^1A_{1g}\rightarrow{}^1A_{2u}$, respectively. The Pt^{II} complexes also gave three bands at 310-320, 350-355 and 420-430 nm assignable to the transitions $^1A_1\rightarrow{}^1B_1$, $^1A_1\rightarrow{}^1A_2$ and $^1A_1\rightarrow{}^3A_2$, respectively. These data indicate a square-planar structure[2-5] for the Ni^{II}, Cu^{II}, Pd^{II} and Pt^{II} complexes.

In the ir spectra of complexes [MLL'] and [MLL'A], no band was observed at 3300-3100 or 3600-3400 cm^{-1}, indicating that hydrogen of the NH group of pyrrole-2-carboxaldehyde and the OH group of acetylacetone get dissociated on complexation. Spectra of the [MLL'] complexes show bands at 1630 cm^{-1} (aldehydic C=O) and 1570 cm^{-1} (C–O) of the acetylacetone. In the ir spectra of the [MLL'A] complexes (in which R=H), the band at 1630 cm^{-1} disappeared and a new band appeared at 1600 cm^{-1} (C=N imine linkage). The band at 1570 cm^{-1} (C=O) of acetylacetone remains unchanged indicating that it does not undergo condensation. The appearance of the band at 3300-3100 cm^{-1} (free N–H) was absent in the mixed ligand complexes derived from alkylamines. The ir spectra of the [MLE.H$_2$O] type complexes showing a band at 3400 cm^{-1} (OH stretch) confirms the presence of water molecule and the band at 1600 cm^{-1} (C=N). The appearence of two new bands at 500-480 and 570-560 cm^{-1} in the above type of complexes suggests the presence of M-O and M-N bondings[6].

On the basis of the above investigations, the [MLL'], [MLL'A] and [MLE.H$_2$O] type complexes may be represented by the structures as shown in Fig. 1.

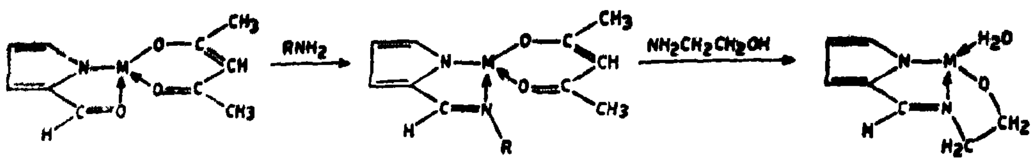


Fig. 1. Structure of mixed ligand complexes.
where M = Ni^{II}, Cu^{II}, Pd^{II} or Pt^{II}
R = H, CH_3 or C_6H_5
E = ethanolamine

Acknowledgement

The authors are thankful to U.G.C., New Delhi for the award of Junior Research Fellowship to one of them (P.M.).

References

1. C. P. Gupta, P. K. Kanungo and R. K. Mehta, *J. Indian Chem. Soc.*, 1979, **56**, 826.
2. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley, New York, 1966, p. 881.
3. L. Sacconi, *J. Inorg. Nucl. Chem.*, 1961, **19**, 73.
4. S. Yamada, *Coord. Chem. Rev.*, 1966, **1**, 415.
5. P. Natarajan and A. W. Adamson, *J. Indian Chem. Soc.*, 1977, **54**, 25.
6. K. Nakamota, "Infrared Spectra of Inorganic and Coordinated Compounds", John Wiley, New York, 1963, p. 151.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 573-576

Solid State Ion-Exchange Properties of Antimonic Acid: Kinetics and Thermodynamics of Li-H Exchange

H. S. RATHORE, ISHTIAQ ALI, R. PRAKASH and MANJU GARG

Chemistry Section, Z. H. College of Engineering & Technology, Aligarh Muslim University, Aligarh-202 001

Manuscript received 22 November 1982, revised 21 September 1983, accepted 17 June 1984

The kinetics and thermodynamics of Li-H exchange on antimonic acid in solid state have been studied. The exchange takes place in two steps and the rate of exchange increases with temperature. The values of diffusion coefficients are comparable to those for exchange on cancrinite in solution. The values of activation energy for diffusion are lower than those for atomic diffusion in metals and for exchange on zeolites in solution. The effect of particle size of antimonic acid, concentration of LiCl and foreign salts, NaCl, KCl, AgCl, $BaCl_2$, $MnCl_2$, Na_2SO_4, K_2SO_4, Na_3PO_4, Na_4SiO_4 on Li-H exchange has been studied. Li^+ is separated from its minerals on antimonic acid in solid state.

CRYSTALLINE antimonic acid is known to be an excellent cation exchanger[1-8]. The ion-exchange mechanism of this compound has not been studied thoroughly. Contradictory statements about its structure and its different affinities for metal ions have been reported[4-9]. An attempt has been made here to study the kinetics and thermodynamics of Li-H exchange on crystalline antimonic acid in solid state. The effects of foreign salts, particle size of antimonic acid and LiCl concentration have been described.

Experimental

Antimonic acid was prepared[5] from $SbCl_5$ (Albright and Wilson).

Ion-exchange between solids: A round bottom flask (250 ml) with an air inlet was connected to a spiral condenser through B-24 joints. The lower end of the condenser was dipped into a beaker containing NaOH solution. Antimonic acid was mixed with a salt and transferred into the flask. The flask was kept in a sand bath at the required temperature. Air was blown continuously into the reaction vessel and the HCl was transferred to the beaker containing NaOH. The content of the beaker were titrated to estimate the acid liberated due to the ion exchange. The radii of fine particles were determined by Cooke's research binocular microscope.

To study the effect of foreign salts on Li-H exchange, antimonic acid (0.5 g) and LiCl (0.1 g) were mixed with varying amounts (0.0-1.0 g) of the foreign salts. In order to determine the ion-exchange capacity antimonic acid (2.0 g) was mixed with LiCl (2.0 g) and the acid liberated in 2 h was collected. The mixture was then taken out, ground in a mortar, placed in the flask and the acid liberated was collected again. The cycle was repeated and the total acid liberated in 6 h was titrated. The effect of particle size was studied by taking antimonic acid of different size (0.5 g. 100-200, 50-100 and 50 mesh) with powdered LiCl (0.2 g). LiCl was taken in varying quantities (0.0-3.0 g) with antimonic acid (1.0 g) for studying the Li^+ concentration effect on Li-H exchange.

Results and Discussion

TG analysis showed the presence of $4H_2O$ per Sb_2O_5 unit[9]. The radii of the exchanger particles were found to be 0.5-0.75 μ. The exchanger (1.0 g) was heated (338-548 K) for 3 h with metal salt (1.0 g of LiCl, NaCl, KCl, AgCl, CuCl, Hg_2Cl_2, $HgCl_2$, $CaCl_2$, $BaCl_2$ and $MnCl_2$) to follow the ion-exchange. The amount of acid liberated was considerable in the case of LiCl while it was negligible in the case of remaining salts. The plot of ion-exchange capacity (K, acid liberated in meq/g of

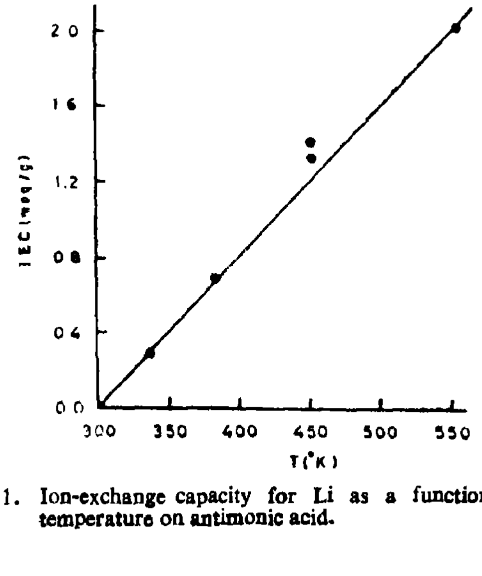


Fig. 1. Ion-exchange capacity for Li as a function of temperature on antimonic acid.

antimonic acid) as a function of temperature is shown in Fig. 1. The value of K for Li-H exchange on antimonic acid is 8×10^{-8} meq g^{-1} K^{-1}. Plots of fractional exchange, F as function of time (t) are shown in Fig. 2. F is defined as

$$F=\frac{\text{the amount of exchange at time t}}{\text{the amount of exchange at infinite time}}$$

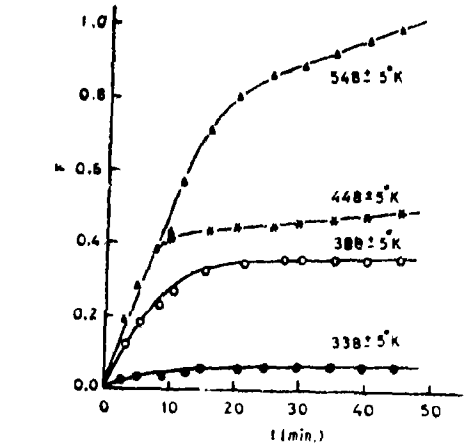


Fig. 2. F as a function of time for Li-exchange on antimonic acid.

As the particle diffusion is the rate controlling step, the theory for particle diffusion[7] can be applied. The fractional exchange, F, at time, t, for particle of radius, r, is given by the expression[7]

$$F=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2Bt),\ \text{where } B=\frac{\pi^2 D_i}{r^2}$$

D_i is the effective diffusion coefficient of Li^+ and H^+ within the exchanger. The values of Bt as a function of F have been tabulated[8]. If the exchange is particle diffusion controlled and D_i is independent of F, a plot of Bt vs. t is a straight line passing through the origin. Its slope will be B and if the particle radius is known, the value of D_i may be calculated. The resulting plots shown in Fig. 3 indicate that exchange takes place in two steps. Both the steps are independent of the concentration of ingoing ions (Li^+) and are particle-diffusion controlled. The slope for both the steps increases as the temperature increases and thus the rate of exchange increases with temperature. It is interesting to note that at 338 K the ion-exchange takes place in one step because the slope for the second step is zero ; at 388 and 448 K ion-exchange takes place in two steps, an initial fast followed by a slow one, at 548 K ion-exchange takes place in two steps, an initial slow followed by a fast one. These facts suggest the existence of two different hydrogen atoms available for ion-exchange within the crystalline antimonic acid. This conclusion finds support from the reported work[9] on crystalline antimonic acid in solution state.

The values of D_i (Table 1) were calculated from the data of Fig. 3. D_i follows the equation[10]

$$D_i=D_0\exp(-Q/RT)$$

TABLE 1—DIFFUSION DATA OF THE Li^+ IN CRYSTALLINE ANTIMONIC ACID

Temp. K		D_i cm^2sec^{-1}	D_0 cm^2sec^{-1}	Q cal mol^{-1}
338	Step I	0.13×10^{-14}	1.3×10^{-9}	4700
	Step II	0	8.4×10^{-7}	6600
388	Step I	12×10^{-14}	–	–
	Step II	0.31×10^{-14}	–	–
448	Step I	18×10^{-14}	–	–
	Step II	1.83×10^{-14}	–	–
548	Step I	19×10^{-14}	–	–
	Step II	70×10^{-4}	–	–

where D_0 is a constant, Q is the activation energy for diffusion, R is the constant (1.987 kcal mol^{-1} K^{-1}), and T is the temperature in K. The values of

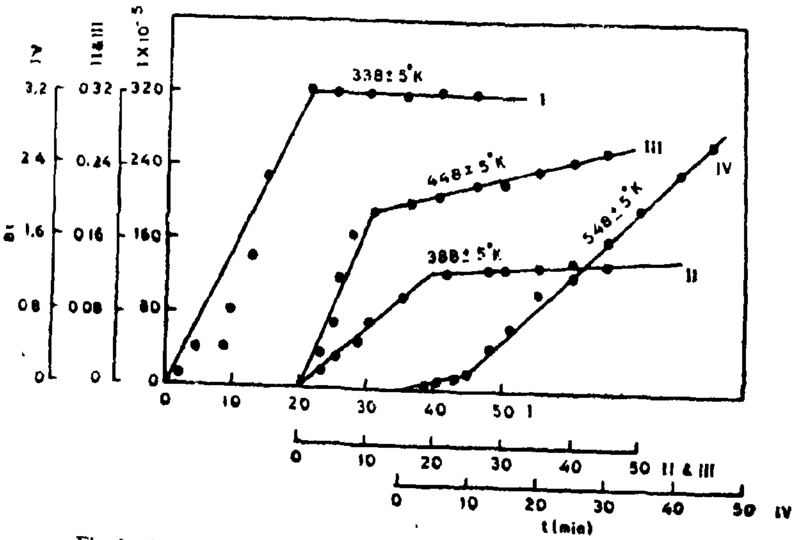


Fig. 3. Bt as a function of time for Li-exchange on antimonic acid.

Q and D_0 were calculated from the plots of log D_t vs. 1000/K. The values for the diffusion coefficient in crystalline antimonic acid are much lower than those for organic resins, thorium dioxide and crystalline zirconium phosphate in solution state[7,8,10,11]. But these values are comparable in magnitude to those of basic cancrinite. Q is lower than that for atomic diffusion in metals[12] and ion-exchange in zeolites. They are comparable to those for the exchange in phenol sulphonic acid resins[10].

Thermodynamics : The effect of LiCl concentration, particle size of antimonic acid and foreign salts on Li-H exchange is shown in Fig. 4 and 6. At 548 K

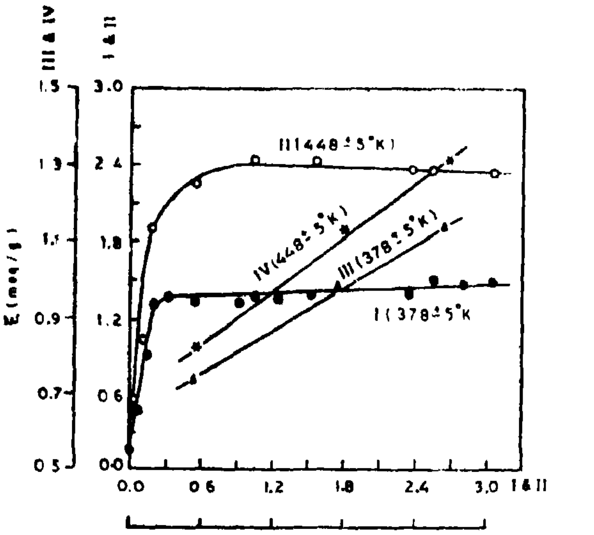


Fig. 4. Effect of LiCl concentration on Li-H exchange on antimonic acid.

the ion-exchange capacity of antimonic acid for Li^+ was found to be 2.87 meq g^{-1}. Ion-exchange isotherms are shown in Fig. 5. The reported procedure was used to compute the thermodynamic parameters[8]. The values are presented in Table 2.

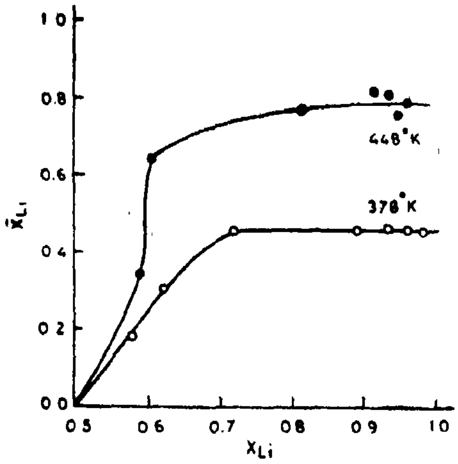


Fig. 5. Isotherms of Li-H exchange on antimonic acid.

TABLE 2—THERMODYNAMIC VALUES FOR THE Li-H EXCHANGE ON ANTIMONIC ACID

Temp. K	$\Delta G°$ kcal mol^{-1}	$\Delta H°$ kcal mol^{-1}	k	$\Delta S°$ cal K^{-1} mol^{-1}
378	0.323	−1.540	0.655	−0.86
448	0.664		0.478	−1.49

Fig. 4 indicates that the exchange of Li increases first and then becomes constant on increasing the concentration of LiCl. Exchange isotherms resembled to those reported[9] for Na-H, Ca-H and Sr-H exchange on antimonic acid in liquid state. It is clear from Fig. 6 that Li-H exchange occurs in presence of foreign salts. In case of Na_3PO_4 and Na_4SiO_4 the amount of acid liberated decreases sharply. It is due to the fact that H^+ produced by Li-H exchange reacts to give H_3PO_4 and H_4SiO_4 and since the boiling point (H_3PO_4=213°) and ionisation constants (H_3PO_4, $k_1=7.5\times10^{-3}$, $k_2=6.2\times10^{-8}$, $k_3=4.8\times10^{-13}$; H_4SiO_4, $k=2\times10^{-10}$) are very high in comparison to that of HCl, the acid liberated remains in the flask and does not come with air. Hence, it seems that antimonic acid can

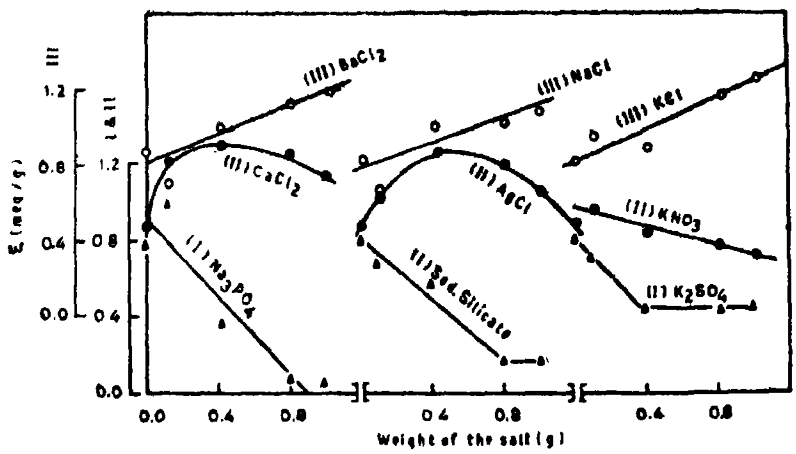


Fig. 6. Effect of some salts on Li-H exchange on antimonic acid at 443±5 K.

be used for the separation of Li from its minerals, namely spodumene, $LiAlSi_2O_6$, amblygonite, $LiAlPO_4F$ etc. Fig. 4 shows that Li-H exchange depends on the particle size and it follows the expression, log p=k. ξ; where p is the mesh size of antimonic acid, k is the constant, and ξ is the *ion-exchange capacity (meq/g) of antimonic acid.* It suggests that the reaction is diffusion-controlled[13].

Thermodynamic parameters in solid state may offer more clear explanation for the ion-exchange. The absence of solvent precludes such factors as hydration, dilution and mixing and it is the ion-exchange process which takes part in solid state. The positive values of $\Delta G°$ indicate that Li^+ has a lower preference for antimonic acid. The negative values of enthalpy suggest that Li^+ is strongly bonded with antimonic acid which finds support from the fact that the heat involved in the course of ion-exchange process[14] is usually small, <2 kcal mol^{-1}. Isotherms show that Li-H exchange increases with temperature while the value of enthalpy is negative. The reason for this ambiguity is that the ion-exchange is diffusion-controlled and diffusion increases as the temperature increases. The negative value of $\Delta S°$ points out that Li-form of antimonic acid is more ordered. These results support the Li-H exchange on antimonic acid in solid state. Therefore, antimonic acid is an important Li selective ion-exchanger.

References

1. M. ABE and T. ITO, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2366.
2. B. G. NOVIKOV, T. G. BEBICHENA, F. A. BELINSKAYA and E. A. MATEROVA, *Vestn Leningr. Univ., Fiz., Khim.*, 1969, 110.
3. V. VESLEY and V. PEKAREK, *Talanta*, 1972, **19**, 219.
4. C. B. AMPHLETT. "Inorganic Ion Exchangers", Elsevier, 1964, pp. 66, 129.
5. H. REMY, *Z. Anorg. Chem.*, 1921, **116**, 255.
6. M. QURESHI, R. KUMAR and H. S. RATHORE, *Talanta*, 1972, **19**, 1377.
7. G. E. BOYD, A. W. ADAMSON and L. S. MYRESS, *J. Am. Chem. Soc.*, 1947, **69**, 2836.
8. D. E. CONWAY, J. H. S. GREEN and D. REICHENBERG, *Trans. Farad. Soc.*, 1954, **50**, 511.
9. L. H. BAESTLE and D. HUYS, *J. Inorg. Nucl. Chem.*, 1968, **30**, 639.
10. G. H. NANCOLLAS and R. PETERSON, *J. Inorg. Nucl. Chem.*, 1961, **22**, 259.
11. D. REICHENBERG, *J. Am. Chem Soc.*, 1953, **75**, 589.
12. L. H. VAN VLACK, "Elements of Material Science", 2nd ed., Addison-Wesely Pub. Co., London, 1968, p. 105.
13. R. P. RASTOGI, P. S. BASSI and S. L. CHADHA, *J. Phys. Chem.*, 1963, **67**, 2569.
14. F. HELFFERICH, "Ion Exchange", McGraw-Hill, New York, 1962.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 577-580

Kinetics and Mechanism of Acid Hydrolysis of Di-6-bromo-2,4-dichlorophenyl Phosphate

H. M. GUPTA and S. PRABHA*

School of Studies in Chemistry, Jiwaji University, Gwalior-474 002

Manuscript received 13 January 1983, revised 28 December 1983, accepted 17 June 1984

Hydrolysis of di-6-bromo-2,4-dichlorophenyl phosphate has been pursued in HCl (0.03-7M) in dioxan water (16%) at 90°. Ionic strength data upto 3μ, requires the participation of neutral (I) as well as conjugate acid (II) forms. The slopes exhibit a fixed contribution irrespective of the value of μ. Unimolecular behaviour for the neutral form has been decided by temperature effect studies. Unusual presence of (I) alone has also been highlighted beyond 4M, where the maximum appears as usual. II, however, hydrolyses bimolecularly via monoester formation. Mirror method calculation are helpful to eliminate monoester formation during acid hydrolysis. Solvent isotope effect study favours specific acid catalysis. The diester involves P-O bond rupture which is strengthened by comparative kinetic data.

KINETIC study of the hydrolysis of di-6-bromo-2,4-dichlorophenyl phosphate has been made for its mechanistic details in the mineral acid range 0.03 to 7 M HCl at 90°, in 16% dioxan-water (for solubility reasons). Concentration of the diester was maintained as $5 \times 10^{-4} M$ throughout the kinetic investigations. First-order rate coefficients have been evaluated using integrated form of the corresponding rate equation. Estimation of the progressive formation of inorganic phosphate as one of the final products during hydrolysis of the present diester was carried out colorimetrically by Allen's modified method[1]. In the present paper, the nature of acid catalysis, types of participating reactive species and their modes of hydrolyses have been discussed and the most plausible routes proposed on the basis of available kinetic data. Various correlation plots have also been used to support the tentative routes of hydrolysis.

Experimental

6-Bromo-derivative of 2,4-dichlorophenol was prepared following the method of Fox and Turner[2]. 6-Bromo-2,4-dichlorophenol (5 g) was then dissolved in dry benzene (10 ml) and PCl_5 (2.15 g) was added to it gradually in the ratio 2 : 1 (w/w) with continuous stirring for nearly 10 h. Subsequent steam distillation of benzene from the reaction mixture left a white solid residue. The residue was dissolved in NaOH (5%) and reprecipitated with HCl (2N). The unreacted phenol was removed by petroleum ether (b.p. 60-80°) and finally the solid recrystallised from CCl_4 yielded pure diester, m.p. 213° (Found : C, 26.89 ; H, 1.42 ; P, 5.67. Requires C, 26.38 ; H, 0.92 ; P, 5.67%).

All reagents used were of AnalaR or Sarabhai (GR) quality.

Results and Discussion

The first-order rate coefficients for the hydrolysis of the present diester in the range 0.03 to 7M HCl are found to increase with the increase in acid upto 4 M (Table 1). At this characteristic[a] acid molarity (4 M) it exhibits a maximum rate which may be ascribed to the presence of increased percentage of singly protonated form of the diester. The rates pass through a minimum at 0.1M where maximum cleavage of neutral form occurs, beyond 4 M the rates decrease.

TABLE 1—OBSERVED AND CALCULATED RATE COEFFICIENTS FOR THE HYDROLYSIS OF DI-6-BROMO-2,4-DICHLOROPHENYL PHOSPHATE AT 90°

HCl M	$10^3 K_{H^+}C_{H^+}$ min^{-1}	$10^3 K_N$ min^{-1}	$10^3 Kc_{calcd}$ min^{-1}	$10^3 Kc_{obs}$ min^{-1}
0.03	–	0.23	0.23	0.24
0.04	–	0.23	0.23	0.25
0.05	–	0.24	0.24	0.28
0.10	–	0.24	0.24	0.26
0.20	0.20	0.26	0.46	0.50
0.30	0.30	0.27	0.57	0.59
0.40	0.40	0.29	0.69	0.69
0.50	0.50	0.31	0.81	0.83
1.00	1.00	0.42	1.42	1.32
2.00	2.00	0.76	2.76	2.39
2.50	2.50	1.03	3.53	3.93
3.00	3.00	1.39	4.39	4.29
4.00	4.00	2.53	6.53	6.25
4.50	–	3.42	3.42	3.45
5.00	–	4.62	3.23[a]	3.49
6.00	–	8.43	3.19[b]	2.80
7.00	–	15.38	2.24[c]	2.27

a, b, c – n in $(aH_2O)_n$ is 1, 2 and 3, respectively.

Neutral electrolyte effect study has been performed at different constant ionic strengths using mixtures of HCl and NaCl. The increase in rates

with the increase in acid concentration (Fig. 1) at each ionic strength (μ) indicates specific acid catalysis. This is further supported by the fact that the rates are slightly increased ($K_{D_2}{}^{O}/K_{H_2O}=1.1$) when water is replaced by D_2O. This also suggests a fast pre-equilibrium proton transfer generally observed for acid-catalysed reactions. Neutral rates are subject to a +ve ionic strength effect, since increase in intercepts with increase in μ has been observed (Fig. 1). Constant slopes of the linear curves (Fig. 1) suggest a +ve but constant contribution of ionic strength effect to the acid-catalysed species (Fig. 2). Similar behaviour has

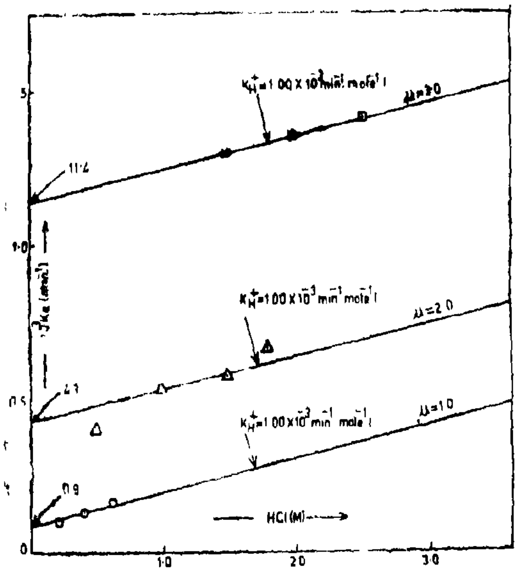


Fig. 1. Hydrolysis of di-6-bromo-2, 4-dichlorophenyl phosphate at constant ionic strengths in 16% dioxan-water at 90°.

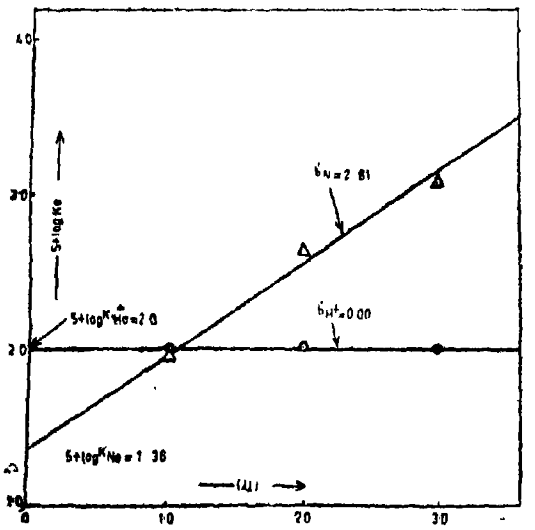


Fig. 2. Hydrolysis of di-6-bromo-2,4-dichlorophenyl phosphate at 90°.

been observed for the acid-catalysed hydrolysis of methyl phosphate[4]. From this neutral electrolyte effect study, the total rates contributed by both neutral and conjugate acid forms have been calculated by the following 2nd empirical term of Debye-Hückel[5] equation.

$$Ke=K_{H^+}.C_{H^+}+K_N$$
$$=K_{HO^+}.C_{H^+}\exp b_{H^+}.\mu+K_{NO}.\exp b_N\mu \qquad (i)$$

where K_{H^+}, K_{HO^+} and b_{H^+} are specific acid-catalysed rate at that ionic strength, specific acid-catalysed rate at zero ionic strength and constant, respectively. Similarly, K_N, K_{NO} and b_N are specific neutral rate at that ionic strength, specific neutral rate at zero ionic strength and constant, respectively (Table 1).

Between 0.03 to 0.1M, the rates agree closely and are contributed by only neutral form in equation (i), of the diester. In the range 0.2 to 4M HCl, the close concordance is due to the contribution of both the neutral and conjugate acid species. The maximum at 4M shows incomplete protonation of the diester suggesting its moderately basic nature. Beyond 4.5 M, the calculations are based on the following modified equation of Bronsted-Bjerrum[6] type using water activity term and considering the participation of the neutral form only.

$$Ke=K_{NO}\exp b_N\,\mu\,(aH_2O)_n \qquad (ii)$$

Beyond 4M, the lowering may be attributed to the total absence of the contribution due to the more reactive conjugate acid form and this can be accounted for by the extensive contribution of only neutral form (less reactive) of the diester. Decrease[6] in water activity with increase in acid molarity may also be responsible for such a decline in rates.

The high magnitude of Arrhenius parameters[7] (Table 2) favours a unimolecular pathway of hydrolysis for the contributory neutral form involving the transition state of highly polar nature. The +ve value of entropy may be understood in terms of steric blocking due to the bulky ortho-bromo substituents coming closer together in two aryl matrices (structure A) due to free rotation about a single bond. Another possibility is the

TABLE 2—CALCULATED ARRHENIUS PARAMETERS IN THE ACID RANGE

HCl M	E kcal mol^{-1}	A sec^{-1}	$\Delta S^{\neq}$ e.u.	$\Delta G^{\neq}$ kcal mol^{-1}
0.5	34.99	1.00×10^{16}	+13.16	+30.21
3.0	36.61	3.82×10^{17}	+20.92	+32.68
4.0	33.72	2.30×10^{16}	+13.71	+28.73
5.0	35.43	1.35×10^{17}	+17.30	+29.15

stabilisation of the diester due to hydrogen bonding (structures B, C and D), blocking way of the entering nucleophile, water (Chart 1).

Solvent effect studies (Ke=13.37$\times10^{-3}$ min^{-1} in 56% dioxan at 4M) as well as Hammond's postulate[8] also favour a more polar transition state[9]. Dioxan-water mixtures being better proton-donating[10]

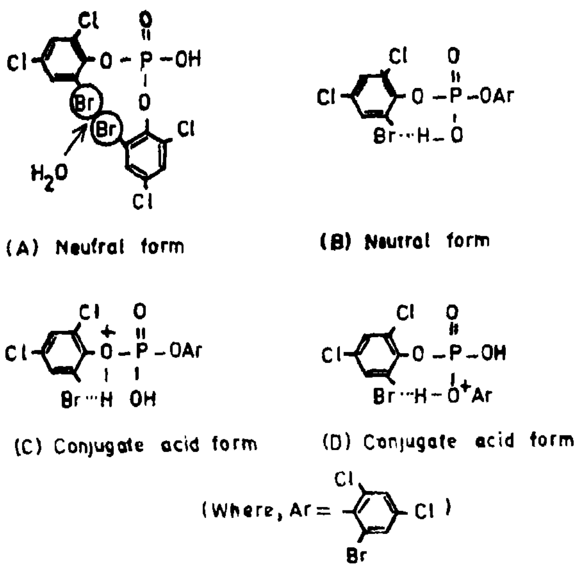


Chart 1

media than water alone will, therefore, increase the rates by stabilising 6-bromo-2,4-dichloro phenoxide ions formed during unimolecular hydrolysis of the neutral form.

The hydrolysis of the present diester follows first-order kinetics as the rates at 4*M* are found to remain unaltered by varying the concentration to either half ($Ke = 6.26 \times 10^{-3}$ min^{-1}) or double ($Ke = 6.30 \times 10^{-3}$ min^{-1}) the normal concentration ($5 \times 10^{-4} M$).

Hammett[11] (0.54), Zücker-Hammett[12] (1.1) and Bunnett[8] (w=8.0 and w*=2.6) plots (not shown) are in favour of a bimolecular pathway for the conjugate acid form. Bunnett-Olsen[13] parameters ϕ as 1.63 (>0.58) suggests that water acts as a proton transfer agent too. Hydration parameter[14] treatment (r=1.36) based on available H_0 data, requires the interference of at least one water molecule leading to the formation of a transition state during hydrolysis. Hammett-Taft[15] relationship plot data ($\rho = +0.72$) recommends electron-withdrawal (−I) by halogens (Br and Cl) present in the diester. This perturbation is also evident from the order of acid-catalysed rates (Table 3) and suggests that the diester hydrolyses largely as its undissociated form. Isokinetic relationship[10] plot (not shown) with β=215.5K and comparative kinetic data (Table 3) combined with above data support bimolecular mechanism for the conjugate acid form, involving P-O bond rupture. P-O

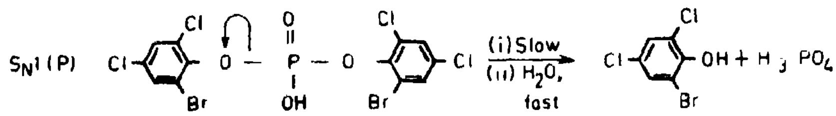


Chart 2—Unimolecular heterolysis of the neutral form.

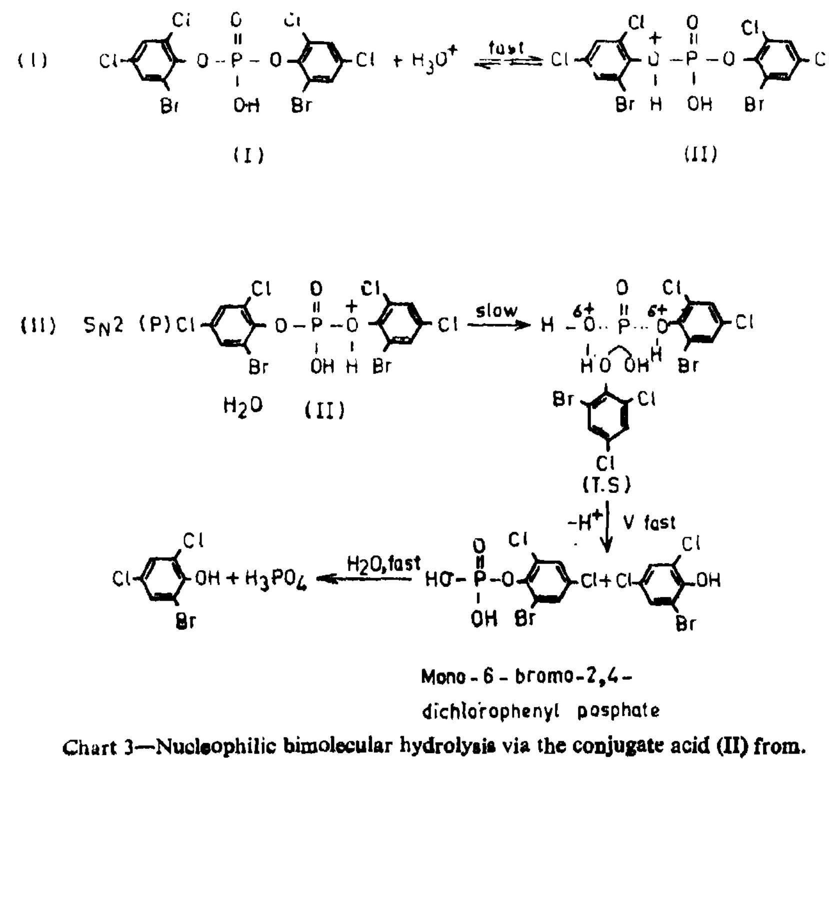


Chart 3—Nucleophilic bimolecular hydrolysis via the conjugate acid (II) from.

TABLE 3—COMPARATIVE KINETIC DATA FOR THE HYDROLYSIS OF HALOGEN SUBSTITUTED DIPHENYL PHOSPHATE ESTERS

Sl. no.	Diesters	Temp. °C	$10^{6}K_{H_3O^+}$ sec^{-1}	Maxima HCl *M*	E kcal mol^{-1}	$-\Delta S^{\ne}$ e. u.	Fission
1.	Phenyl[a]	100	–	4*	20.8	27.9	P–O†
2.	*p*-Cl[b]	80	6.93	4*	10.6	65.0	P–O
3.	*p*-Br[c]	98	0.22	4.5*	20.1	30.0	P–O
4.	2,4-di-Cl[d]	98	4.30	3.5	16.6	33.9	P–O
5.	2,4,6-tri-Cl[e]	90	3.03	2.5	34.4	11.9	P–O
6.	2,4,6-tri-Br-[f]	98	4.40	4	26.1	7.1	P–O
7.	6-Br-2,4-di-Cl[g]	90	1.70	4	33.7	–13.7	P–O

* $HClO_4$. † Fission determined experimentally.

[a] Ref. 6. [b] S. Deobhakta, Ph.D. Thesis, Jiwaji University, 1968. [c] M. M. Mhala, M. D. Patwardhan and G. Kasturi, *Indian J. Chem.*, 1969, 7, 149. [d] S. S. Bhatwadekar, Ph.D Thesis, Jiwaji University, 1972. [e] A. Chaturvedi, Ph.D. Thesis, Jiwaji University, 1981. [f] S. Chaudhari, Ph.D. Thesis, Jiwaji University, 1947. [g] This work.

fission leads to the formation of substituted phenoxide ions as stable intermediates.

Lastly, at low acid molarity the rates calculated by mirror method[6] (0.30×10^{-3} min^{-1} at $0.1M$) closely resemble the experimentally observed rates (0.26×10^{-3} min^{-1}) for the diester suggesting the absence of monoester formation during its hydrolysis. Similar calculations when tried at a higher acid molarity, $3M$, yield intermediate value of rate data, indirectly pointing out the hydrolysis of conjugate acid form to proceed via monoester formation. Thus the hydrolysis of the diester proceeds in the two ways via two reactive species (Charts 2 and 3).

Acknowledgement

One of the authors (H.M.G.) is grateful to U. G. C., New Delhi for awarding a junior research fellowship.

References

1. R. J. L. ALLEN, *Biochem. J.*, 1940, **34**, 858.
2. D. L. FOX and E. E. TURNER, *J. Chem. Soc.*, 1930, 1861.
3. J. F. BUNNETT, *J. Am. Chem. Soc.*, 1961, **83**, 4956.
4. C. A. VERNON, *Chem. Soc., Spec. Publ.*, 1957, **8**, 24.
5. F. A. LONG and W. F. MCDEVIT, *Chem. Rev.*, 1952, **51**, 119.
6. P. W. C. BARNARD, C. A. BUNTON, D. KELLERMAN, M. M. MHALA, B. SILVER, C. A. VERNON and V. A. WELCH, *J. Chem. Soc.*, 1966, 227, 229.
7. S. Z. ARRHENIUS, *Phys. Chem.*, 1889, 4, 226.
8. G. S. HAMMOND, *J. Am. Chem. Soc.*, 1955, **77**, 2444, 2549.
9. C. K. INGOLD, "Structure and Mechanism in Organic Chemistry", Bell and Sons, London, 1953, p. 345.
10. J. R. COX and O. B. RAMSAY, *Chem. Rev.*, 1964, **64**, 317.
11. L. P. HAMMETT, "Physical Organic Chemisty", McGraw-Hill, London, 1940, p. 335.
12. L. ZÜCKER and P. HAMMETT, *J. Am. Chem. Soc.*, 1932, **61**, 2791.
13. J. F. BUNNETT and F. P. OLSEN, *Can. J. Chem.*, 1966, **44**, 1917.
14. K. YATES and R. A. MCCLELAND, *J Am. Chem. Soc.*, 1967, **89**, 2686.
15. JACK HINE, "Physical Organic Chemistry", 2nd ed., McGraw-Hill, 1962, pp. 93-103.
16. R. D. GILLIOM, "Introduction to Physical Organic Chemistry", Addison Wesley Pub., 1970, pp. 167-169.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 581-583

Kinetics of Oxidation of Glycollic Acid by Chromium Peroxydichromate

N. D. VALECHHA* and D. S. DAKWALE

Department of Chemistry, Govt. Science College, Rewa-486 001

Manuscript received 25 August 1983, revised 15 February 1984, accepted 26 May 1984

The kinetics of oxidation of glycollic acid by chromium peroxydichromate has been studied. At low concentration of the substrate the order of reaction is pseudo zero and one with respect to oxidant and substrate, however, at high concentration of the substrate the respective orders are one and two. The product of oxidation is found to be formaldehyde. Influence of temperature, acids, neutral salts, Mn^{II} and Cr^{III} ions and solvent has been studied. A tentative mechanism has been suggested.

OXIDATION of glycollic acid has been studied with different oxidants[1-12]. However, no attempt has been made to study its kinetics by chromium peroxydichromate (CPD). In this paper the kinetic study of glycollic acid by chromium peroxydichromate is presented. The results have been compared with those of the other oxidants.

Experimental

Glycollic acid (Riedel) and all other chemicals were of A. R. quality. Chromium peroxydichromate was prepared by a known method[13]. The solutions of the reactive substances were brought to the required temperature (±0.1°) in a thermostat, and then rapidly mixed. Aliquots were withdrawn at known intervals of time and the reaction was stopped by adding ice cold distilled water. The unreacted chromium peroxydichromate was estimated iodometrically.

Results and Discussion

At low concentration of the substrate, the order of reaction is pseudo zero and one with respect to oxidant and substrate, respectively. However, at high concentration of the substrate the respective orders are one and two (Table 1 and 2).

TABLE 1—EFFECT OF VARYING CONCENTRATION OF SUBSTRATE

[CPD] = 0.0166 *N* Temp. = 40°

[GA]	$10^n k_0$ equiv l^{-1} min^{-1}	$\frac{10^4 k_0}{[GA]}$ min^{-1}	$10^3 k_1$ min^{-1}	$\frac{10^3 k_1}{[GA]^2}$ l^2 $equiv^{-2}$ min^{-1}
0.10	2.51	2.51	–	–
0.20	5.10	2.55	–	–
0.30	8.09	2.69	–	–
0.40	11.54	2.86	–	–
0.80	–	–	12.86	2.09
1.00	–	–	19.73	1.97
1.25	–	–	31.53	2.01

TABLE 2—EFFECT OF VARYING CONCENTRATION OF CPD

$[CPD] \times 10^3$ *N*	[GA] = 0.2 *N* $10^4 k_0$ equiv l^{-1} min^{-1}	[GA] = 0.8 *N* $10^3 k_1$ min^{-1}
0.83	2.07	1.54
1.00	2.52	1.63
1.25	3.38	1.58
1.66	5.10	1.65
2.50	8.50	1.67
5.00	22.10	1.64

At low concentration of the substrate plot of x *vs* time is a straight line, while at high concentration of the substrate plot of log (a-x) *vs* time is a straight line, indicating that the order with respect to CPD is pseudo zero and one respectively. Pseudo zero order rate constant increases with increase in the concentration of CPD, while first order rate constant is independent of the initial concentration of the oxidant.

Effect of temperature : Kinetics of oxidation of glycollic acid by CPD has been studied at different temperatures. Plot of log k *vs* 1/T is linear. Energy of activation (△E), entropy of activation (ΔS^{*}) and free energy of activation (ΔG^{*}) have been calculated and are recorded in Table 3.

TABLE 3—THERMODYNAMIC PARAMETERS

△E k cal mol^{-1}	ΔS^{*} e. u.	ΔG^{*} k cal mol^{-1}
11.003	−51.35	27.72

Effect of acids : It is observed that in the presence of HCl or H_2SO_4 the reaction rate increases and further increases with increase in the concentration of the added acid (Table 4). The reason for this enhancement is that due to common ion effect the dissociation of glycollic acid is suppressed, so neutral molecule of glycollic acid is involved in the rate-determining step. If glycollate

anions were involved in the reaction then the rate would have decreased in the presence of an acid.

TABLE 4—EFFECT OF HCl AND H_2SO_4 ON THE REACTION RATE

[CPD] = 0.0166 N [GA] = 0.30 N Temp. = 40°

[Acid] N	$10^4 k_o$ equiv l^{-1} min^{-1}
0.000	8.09
0.010	9.97 (9.43)
0.020	12.65 (9.88)
0.025	13.62 (11.10)
0.050	21.98 (16.26)

Values in parenthesis are in the presence of H_2SO_4.

The data in Table 4 reveal that the presence of HCl accelerates the reaction rate more than H_2SO_4 at equinormal concentration. The reason being that HCl is relatively of greater strength than H_2SO_4 and, therefore, produces more H^+ at equinormal concentration. The presence of HCl will supress the dissociation of glycollic acid more than H_2SO_4. Hence, HCl accelerates the reaction rate more than H_2SO_4.

Effect of neutral salts: It is observed that chlorides and sulphates of sodium and potassium have nearly no effect on the reaction rate at low ionic strength. This suggests that one of the reactants is a neutral molecule in the rate-determining step.

Effect of solvent: To study the effect of solvent, the oxidation of glycollic acid was carried out in varying percentage of acetic acid-water mixture. The rate of oxidation was found to increase with the increase in the percentage of acetic acid in the reaction mixture (Table 5). The plot of log k vs 1/D is linear with a positive slope, indicating that the reaction is of a positive ion-dipole type.

TABLE 5—EFFECT OF SOLVENT

[GA] = 0.20 N [CPD] = 0.01667 N Temp. = 40°

HOAc-Water (v/v)	Dielectric constant	$10^4 k_o$ equiv l^{-1} min^{-1}
00-100	73.13*	5.10
10-90	66.07	7.27
20-80	59.64	9.51
30-70	53.48	11.84
40-60	46.31	15.50
50-50	39.62	20.81

* Calculated from the relation $\log \epsilon = 1.9461 - 0.00205 \times t$

Effect of Mn^{II} ion: It is observed that in the presence of Mn^{II} ions the reaction rate is retarded (Table 6). This is expected if Mn^{II} ions catalyse the disproportionation of intermediate valence state of chromium and indicates that Cr^{IV} is probably involved as an intermediate.

Effect of Cr^{III} ion: It is observed that in the presence of added Cr^{III} ions the reaction is retarded (Table 7). The reason being that Cr^{III} ions possibly form complex with glycollic acid. Thus the decrease in the concentration of glycollic acid lowers the value of the rate constant.

TABLE 6—EFFECT OF Mn^{II} IONS

[GA] = 0.30 N [CPD] = 0.0166 N Temp. = 40°

Mn^{2+} $\times 10^3$ M	$10^4 k_o$ equiv l^{-1} min^{-1}
0.0	8.09
1.0	7.68
2.0	7.51
4.0	7.32

TABLE 7—EFFECT OF Cr^{III} IONS

[GA] = 0.30 N [CPD] = 0.0166 N Temp. = 40°

[Cr^{III} acetate. H_2O] $\times 10^3$ M	$10^4 k_o$ equiv dm^{-3} min^{-1}
0.0	8.09
5.0	7.81
7.5	7.69
10.0	7.53

The product of oxidation in excess substrate concentration is formaldehyde, which has been identified by preparing its dimedone derivative[14] and by its characteristic spot test[15].

Mechanism: Chromium peroxydichromate is known to decompose in aqueous solution as

$$Cr_2(Cr_2O_8)_3 \xrightarrow{\text{fast}} 2\,Cr^{3+} + 3Cr_2O_7^{2-} + 3O \qquad \text{(i)}$$

Peroxy-oxygen oxidises glycollic acid rapidly. The oxidation of glycollic acid by peroxy-oxygen is followed by slow oxidation with hexavalent chromium of dichromate ion.

$$CH_2OHCOOH + O \xrightarrow{\text{fast}} CH(OH)_2COOH \xrightarrow[-H_2O]{\text{fast}} CHO\,COOH \xrightarrow[-CO_2]{\text{fast}} HCHO \qquad \text{(ii)}$$

$$CH_2OH.COOH + Cr^{6+} \xrightarrow[k]{\text{slow}} \underset{\text{(unstable)}}{CH(OH)_2COOH} + Cr^{4+} \qquad \text{(iii)}$$

$$CH(OH)_2COOH \xrightarrow[-H_2O]{\text{fast}} CHOCOOH \xrightarrow[-CO_2]{\text{fast}} HCHO \qquad \text{(iv)}$$

$$Cr^{4+} + Cr^{4+} \xrightarrow{\text{fast}} Cr^{5+} + Cr^{3+} \qquad \text{(v)}$$

$$CH_2OHCOOH + Cr^{5+} \xrightarrow{\text{fast}} \underset{\text{(unstable)}}{CH(OH)_2COOH} + Cr^{3+}$$

$$CH(OH)_2COOH \xrightarrow[-H_2O]{\text{fast}} CHOCOOH \xrightarrow[-CO_2]{\text{fast}} HCHO \qquad \text{(vi)}$$

From the proposed mechanism the derived rate laws are

$$-\frac{d[CPD]}{dt}=k[GA]\,[CPD]^{\frac{1}{2}}$$ for low concentration of substrate

and $$-\frac{d[CPD]}{dt}=k^1[GA]^2[CPD]$$ for high concentration of substrate

These rate laws are in agreement with the experimental observations.

Thermodynamic parameters and kinetic process: The rate of reaction is not determined solely by the energy of activation ($\triangle E$), since the frequency factor can vary over a considerable range. It is the free energy of activation ($\triangle G^{+}$), which determines the rate of reaction at a given temperature. Higher the $\triangle G^{+}$, the slower is the reaction rate[16] at a given temperature. If entropy of activation (ΔS^{+}) is negative, the activated complex is less probable and the rate is slower[17]. Thus the large negative entropy of activation and high free energy of activation (Table 3) mean a slow reaction, which is in agreement with the observed smaller specific rate constant. The negative value of $\triangle S^{+}$ indicates the reaction should be between similarly charged ions or between a charged ion and a neutral molecule[18]. Thus the calculated thermodynamic parameters explain the kinetic process.

Comparison of kinetics and mechanism of glycollic acid oxidation by CPD with other oxidants: The order of reaction between glycollic acid and CPD is pseudo zero and one with respect to oxidant and substrate, respectively at low concentration of the substrate, while at high concentration of the substrate the respective orders are one and two. However, with other oxidants the order of reaction is one with respect to both the oxidant and the substrate. The entropy of activation for the reaction investigated is large negative (Table 3), while with most of the other oxidants it is either positive or small negative.

The present investigation reveals that the change in ionic strength has nearly no effect on the rate of reaction in dilute solution. However, in case of most of the other oxidants the change in ionic strength has a definite retarding influence on the reaction rate.

The effect of dielectric constant of the medium was studied with a limited number of oxidants. In chromic acid[3] oxidation of glycollic acid, no relationship between logarithm of rate constant and dielectric constant of the medium was established. In lead tetra-acetate[9] oxidation of glycollic acid, on the basis of effect of dielectric constant on the reaction rate, the reaction of dipole-dipole type was suggested. However, the effect of dielectric constant on the rate of oxidation of glycollic acid by CPD shows that the reaction is of a positive ion-dipole type.

Oxidation of glycollic acid with some oxidants showed a kinetic evidence regarding the complex formation between glycollic acid and the oxidising species. However, no such evidence was observed for the present reaction as Michael Menton's plot of $1/k$ *vs* $1/[GA]$ does not give a positive intercept on Y axis.

The product of oxidation of glycollic acid by CPD is formaldehdye, while with the other oxidants it was found to be either glyoxalic acid or oxalate ion or formic acid or formaldehyde.

The mechanism of oxidation of glycollic acid by other oxidants[1,2,4,7] involved either rupture of α-C-H bond or rupture of C-C bond in the rate-determining step. In case of some oxidants[19-21] the slow step involved the decomposition of the complex into free radicals. However, the proposed mechanism of oxidation of glycollic acid by chromium peroxydichromate involves two electron transfer from the reductant, glycollic acid, to the oxidising species, Cr^{VI} in the rate-determining step. The proposed mechanism is, however, similar to that suggested for the oxidation of lactic acid by chromium peroxydichromate[23].

References

1. G. V. Bakore and A. A. Deshpande, *Z. Phys. Chem.*, 1964, 227, 14.
2. K. K. Sengupta, A. K. Chatterjee and S. P. Moulik, *Bull. Chem. Soc. Jpn.*, 1970, 43, 3841.
3. G. V. Bakore, R. Dayal and P. Nath, *Z. Phys. Chem.*, 1964, 227, 19.
4. R. Dayal, K. K. Banerjee and G. V. Bakore, *Indian J. Chem.*, 1971, 9, 1017.
5. Mc Auley, *J. Chem. Soc.*, 1965, 4054.
6. G. V. Bakore and S. N. Joshi, *Proc. Indian Acad. Sci.*, 1971, 73, 198.
7. V. Lal, V. N. Singh, H. S. Singh and M. P. Singh, *Indian J. Chem.*, 1972, 10, 392.
8. K. K. Sengupta, D. K. Khamrui and D.C. Mukherjee, *Indian J. Chem.*, 1975, 13, 348.
9. K. Swaminathan, S. Sundaram and N. Venkatasubramanian, *Indian J. Chem.*, 1975, 13, 1163.
10. B. L. Chandwani and G. D. Menghani, *Indian J. Chem., Sect. A*, 1977, 15, 560.
11. K. K. Banerjee, *Indian J. Chem., Sect. A*, 1977, 15, 615.
12. S. P. Mushran, M. C. Agarwal and B. J. Prasad, *J. Chem. Soc.*, 1971, 712.
13. D. Singh and R. C. Rai, *J. Indian Chem. Soc.*, 1970, 47, 239.
14. F. G. Mann and B. C. Saunders, "Practical Organic Chemistry", 4th ed., Longmans, London. 1960, pp. 145, 277.
15. F. Feigl, "Spot Tests in Organic Analysis", Elsevier, Amsterdam, 1956, p. 331.
16. S. Glasstone and D. Lewis, "Elements of Physical Chemistry", 2nd ed., Macmillan Press, London, 1960, p. 633.
17. S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941, p. 418.
18. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", John Wiley, 1963, p. 143.
19. P. Levesley and W.A. Waters, *J. Chem. Soc.*, 1955, 217.
20. W. A. Waters, J. R. Jones and J. S. Littler, *J. Chem. Soc.*, 1961, 630.
21. T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 1964, 1192.
22. D. K. Khamrui, D. C. Mukherjee and K. K. Sengupta, *Indian J. Chem.*, 1975, 13, 1288.
23. R. P. Srivastava and R. C. Rai, *J. Indian Chem. Soc.*, 1972, 49, 625.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 584-585

Potentiometric Studies on the Complexes of Some Transition Metal Ions and Rare-Earth Ions with 3-Phenyl-2-thio-2,4, (1*H*, 3*H*) quinazolinedione

DEEPAK H. RAHEJA, (Mrs.) USHA P. FULWADHVA and N. B. LAXMESHWAR*

Physical Chemistry Laboratory, Institute of Science, Bombay-400 032

Manuscript received 5 October 1983, accepted 30 May 1984

Complexation equilibrium of metal complexes of Cu^{II}, Zn^{II}, Cd^{II}, Ni^{II}, Mn^{II} and rare-earth metals like Nd^{III} Sm^{III}, Gd^{III} and Dy^{III} with 3-phenyl-2-thio-2,4, (1*H*, 3*H*) quinazolinedione have been studied potentiometrically. The proton dissociation constant of the reagent and the dissociation constant of its metal complexes have been determined by Celvin *p*H titration technique as adopted by Irving and Rossotti at 27±0.1° and at ionic strength, $\mu = 0.1M$ in 3 : 1 (v/v) dioxane-water medium. The order of stability constants of the complexes is found to be $Cu^{II} > Cd^{II} > Ni^{II} > Zn^{II} > Mn^{II}$. The stability constants in case of rare-earth metal ions have been investigated only to know their ionic character.

2-THIO-2,4, (1*H*, 3*H*) quinazolinedione and its substituted derivatives are heterocyclic compounds having allied structures with those of thioxoimidazolidinones (2-thiohydantoins). In the present investigation the compound is prepared with the idea to use it as complexing agent. In the ligand molecule proton dissociation takes place because of the presence of tautomeric form of the ligand, giving rise to thiol group and thus the complexation with metal ion is possible. This type of tautomeric form in such compounds is already reported in the literature by ir spectral studies.

Experimental

The ligand 3-phenyl-2-thio-2, 4, (1*H*, 3*H*) quinazolinedione was synthesised by standard methods[1,2] and recrystallized from acetic acid yielded colourless plates, m.p. 301°. The structure of the ligand molecule is confirmed by ir spectral analysis. Dioxan used was purified by standard method[3]. Distilled water was used throughout the investigation.

The free acid, free acid plus ligand and the mixture of metal containing the ligand and the acid were titrated against standard carbonate-free sodium hydroxide (0.1*M*). The solutions of metal perchlorates were prepared from A.R. grade oxide and carbonate, and standardised by EDTA titrations[4]. The potentiometric titrations were carried out in an inert atmosphere by bubbling oxygen-free nitrogen gas through the solution. All the measurements were carried out at 27±0.1° in 3 : 1 (v/v) dioxane-water medium.

Results and Discussion

$\bar{n}_A$ values were obtained by using Irving and Rossotti equation and then *p*K value for reagent calculated. This value is confirmed by plot of *p*H *vs* $\bar{n}_A$ and *pH vs* $\log \bar{n}_A/(1-\bar{n}_A)$ as shown in Fig. 1.

3-Phenyl-2-thio-2,4, (1*H*, 3*H*) quinazolinedione has been reported for the complexation with Pb^{II} in solid state[5]. This clearly indicates that the complexation has taken place through sulphur after the dissociation of proton from SH group. On this basis the present investigation of the stoichiometric metal-ligand stability constant of 3-phenyl-2-thio-

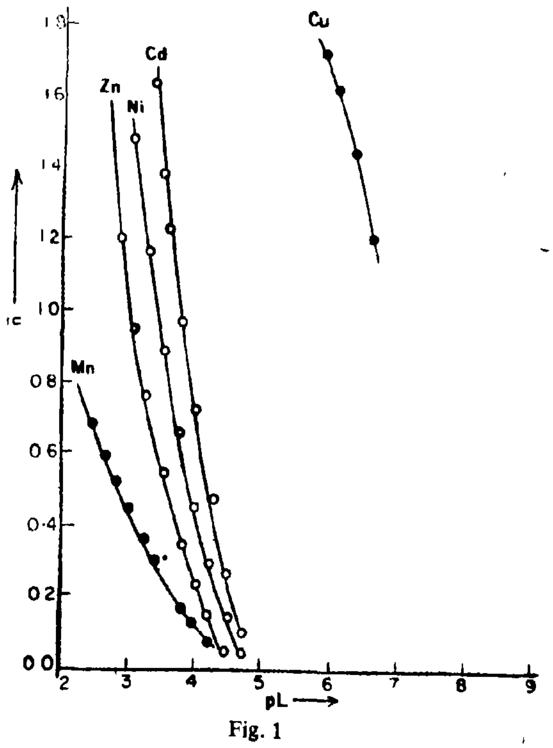


Fig. 1

*Part of the paper presented at the Annual Convention of Chemists, Madras, 29th December, 1981.

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES

Temp. = 27±0.1° μ = 0.1 *M*

	H^+	Cu^{II}	Cd^{II}	Ni^{II}	Zn^{II}	Mn^{II}	Sm^{III}	Gd^{III}	Dy^{III}	Nd^{III}
log K_1	7.54	–	4.20	3.93	3.55	2.90	4.60	4.75	4.80	4.85
log K_2	–	6.22	3.55	2.90	2.65	–	3.65	3.71	3.65	3.85

2,4, (1*H*, 3*H*) quinazolinedione with transition metal ions and rare-earth metal ions is reported for the first time.

The value of $\bar{n}$ (average number of ligand molecule attached per metal ion) and *p*L (free ligand exponents) were calculated applying Irving and Rossotti method[6]. The plot of $\bar{n}$ *vs* *p*L gave the formation curve of metal complexation equilibria (Fig. 2).

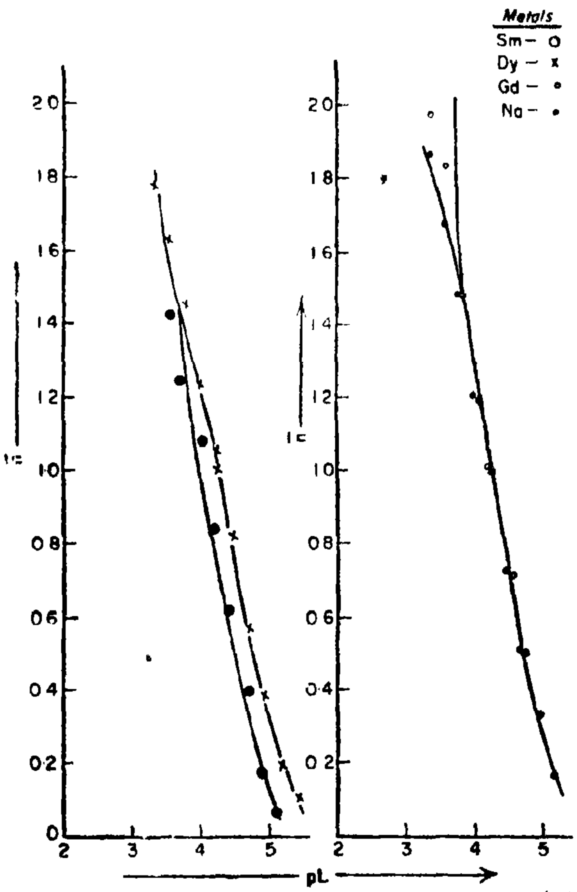


Fig. 2. Graph of $\bar{n}$ against *p*L.

The formation curves were used to determine log K_1 and log K_2 by half integral method. The curves obtained are fairly symmetrical in nature in all the cases. In some cases log K_2 values were obtained by extrapolation. Where the difference between log K_1 and K_2 found to be less than 1.78 units, the same were calculated by least square method. Cu^{II} is noticed to form only 1 : 2 complexes. The non-existence of 1 : 1 complex with this metal may be due to the absence of stepwise formation of complex. It is also observed that log K_2 value with this metal ion is very high, which again indicates greater stability of 1 : 2 complex. Limits of error and the standard deviations for log K values are applied and most representative values are recorded in Table 1. The order of stability constant for transition metals is found to be $Cu^{II} > Cd^{II} > Ni^{II} > Zn^{II} > Mn^{II}$. This order of stability is in agreement with the order reported earlier.

As regards to the stability order of complexes for rare-earth metals, it is expected to get a gradual increase in stability with increase in atomic number because of the well known lanthanide contraction. However, it is verified with a few rare-earth metal ions and their values are reported in Table 1.

Acknowledgement

The authors thank Dr. D. G. Vartak, B.A.R.C., Bombay for his valuable suggestions.

References

1. PAR KANYI, *Collect. Czech. Chem. Commun.*, 1963, 26, 998.
2. TH. KAPPE, W. STEIGER and E. ZIEGLER, *Monatsh. Chem.*, 1967, 98, 214.
3. I. A. VOGEL, "A Text Book of Practical Organic Chemistry", 3rd ed., Longmans, London, 1959, p. 117.
4. H. R. FLASCHKA, "EDTA Titration", Pargamon Press, New York.
5. T. N. GHOSH, *J. Indian Chem. Soc.*, 1930, 7, 981.
6. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 586-589

Spectral and Polarographic Behaviour of Ternary Complexes of Copper(II)-Glycylglycine and Some Amino-acids

S. N. MANDLOI, P. K. CHITALE and M. S. VERMA*

School of Studies in Chemistry, Vikram University, Ujjain-456 010

and

H. L. NIGAM

A. P. S. University, Rewa-486 003

Manuscript received 12 April 1983, revised 13 February 1984, accepted 17 June 1984

The mixed ligand complexes of the type [CuAB]X H_2O, (where X = 0 or 2, A = amide deprotonated glycylglycine, B = glycine, alanine, serine, threonine or valine) have been isolated. The formulae of these complexes have been proposed on the basis of elemental analyses. Coordination through amino group of glycylglycine and secondary ligands, deprotonated amide group of glycylglycine and carboxylate group of the amino acids have been investigated on the basis of ir data. Visible spectral studies made on these complexes lead to the conclusion that these are of tetragonally distorted octahedral geometry in aqueous solutions.

Polarographic behaviour of the complexes have been investigated in 0.1 *M* aqueous sodium perchlorate medium. Polarographic characteristics ($E_{\frac{1}{2}}$, i_d, D, slope, α) have been determined. Activation energy of diffusion Q_D has been calculated by Vlček's equation. Values of reference rate constant, K_r, at a reference potential − 0.3 V against SCE have been determined from the characteristics of irreversible waves. The mechanism of electroreduction of the complexes [Cu(gg) (val)] $2H_2O$ and [Cu(gg)(ser)] $2H_2O$ undergoes change with temperature at dropping mercury electrode. A correlation between spectral parameters, ν_{max}, and polarographic parameters ($E_{\frac{1}{2}}$, K_r, Q_D), has been made and anomalies observed have been explained on the basis of steric effects. The data have been rationalized by proposing a mechanism of the electroreduction of the depolariser at the electrode surface on basis of the orientation of the orbitals of the central metal ion and its local symmetry, D_{2h}.

It is being increasingly realized that the transition metal complexes behave characteristically at the dropping mercury electrode and yield information about the lowest vacant orbital. Considering the information about the highest occupied orbital from spectral behaviour of such a system, it would be possible to correlate redox properties of coordination compounds with their spectral parameters. Following this idea, attempts[1-8] have been made to seek correlation of the spectral behaviour *vis-a-vis* electrode characteristics of coordination compounds with some success. The report on ternary complexes, however, is very scanty. In the present communication, such a correlation has been attempted by studying electrode behaviour of some ternary complexes of a biologically important transition metal like copper and biologically important ligands such as glycylglycine as primary ligand and some amino-acids as secondary ligands. Such ternary complexes are important in transport of copper through biological membranes. The complexes studied are [CuAB]X H_2O. where X=0 or 2, A=amide deprotonated glycylglycine, and B=glycine, alanine, serine, threonine or valine.

Equilibrium studies of these complexes have been made by previous workers[9-12] potentiometrically and conclusions have been drawn, concerning the linkages of amino-acids and of glycylglycine to copper(II) ion on the basis of stability constants. No attempt, to the best of the authors' knowledge, has been made to isolate and characterize these complexes. The authors have, therefore, attempted to isolate and characterize [CuAB]X H_2O complexes. The formulae of the complexes have been proposed on the basis of elemental analysis. Infrared and electronic spectral studies revealed these complexes to be of tetragonally distorted octahedral structure in aqueous solutions. A comparison of their redox properties with the spectral parameters has been made. A probable mechanism have been proposed for the reduction of these complexes at electrode surface on the basis of their orientation at the electrode surface and their D_{2h} symmetry.

Experimental

All the complexes were prepared by heating the mixture of an equimolar aqueous solutions of

AnalaR glycylglycine and any one of the secondary ligands, *i.e.* glycine, alanine, serine, threonine and valine with an excess of freshly precipitated copper hydroxide on water bath for 0.5 h. Hot solutions were filtered and concentrated to one-third of its volume. Absolute alcohol was added to the hot solution to get precipitates of the complexes. Precipitates were washed with absolute alcohol and solvent ether. All complexes were dried at 50° and are intense blue in colour. All of the complexes are highly soluble in water and are insoluble in organic solvents like ethanol, benzene and ether.

Carbon, hydrogen and nitrogen in the complexes were estimated by G.D.R. microanalyser. Ir spectra (KBr) were recorded on Perkin-Elmer 377. Electronic spectra of all the complexes were taken in aqueous solution on Beckman 26 spectrophotometer.

For polarographic investigations AnalaR sodium perchlorate was used as a supporting electrolyte. To remove the oxygen from polarographic solution, purified nitrogen gas was bubbled at the rate of two bubbles per sec for 0.5 h. All the polarograms were recorded with the help of a manual polarographic circuit as recommended by Kolthoff and Lingane. All the potentials were measured against Hume and Harris saturated calomel electrode. The cell resistance was measured with the help of an a.c. Wheatstone bridge and was found to be 1000 ± 100Ω. Therefore, ir correction was not needed. The characteristics of dropping mercury electrode were determined at three different heights of mercury column, one set of data is as follows (Table-2): $h_{corr}=58.5$ cm, t=3.8 sec, m=1.5 mg/sec, $m^{2/3}t^{1/6}=1.64$.

Results and Discussion

On the basis of the carbon, hydrogen and nitrogen estimation (Table 1) formulae proposed for the complexes studied are, (I) [Cu(gg) (thr)] $2H_2O$, (II) [Cu(gg) (alan)] $2H_2O$. (III) [Cu(gg) (val)] $2H_2O$, (IV) [Cu(gg) (gly)], (V) [Cu(gg) (ser)] $2H_2O$; where gg=glycylglycine, thr=threonine, alan=alanine, val=valine, gly=glycine, ser=serine.

TABLE 1—ANALYTICAL DATA OF THE MIXED LIGAND COMPLEXES OF COPPER(II)—GLYCYLGLYCINE AND SOME AMINO-ACIDS

No.	Complex	Analysis % ; Found/(Calcd) C	H	N
I.	[Cu(gg)(thr)]$2H_2O$	27.52 (27.86)	5.40 (5.45)	11.95 (12.07)
II.	[Cu(gg)(alan)]$2H_2O$	27.20 (27.27)	5.22 (5.52)	13 50 (13.63)
III.	[Cu(gg)(val)]$2H_2O$	31.52 (31.21)	6.20 (6.07)	12.00 (12.14)
IV.	[Cu(gg)(gly)]	27.02 (26.80)	4.52 (4.09)	15.50 (15.63)
V.	[Cu(gg)(ser)]$2H_2O$	25.80 (25.15)	5.00 (5.09)	12.25 (12.57)

Infrared spectra : Peptides[13] of low molecular weight and amino-acids[14] exist as Zwitterions with an open chain structure. In the ir spectra of the amino-acids and glycylglycine used, the bands at 3070, 2564, 2100, and 1630 cm^{-1} are due to the presence of $-NH_3^+$ group[15]. These bands are found to be absent in the complexes under investigation and two bands appearing at ~ 3320 and 3240 cm^{-1} lead to the conclusion that there is coordination[16] through the amino group of the glycylglycine and amino-acids used in all the cases. The carbonyl group of the peptide link absorbs[17] at 1670 and 1540 cm^{-1} in glycylglycine. These bands shift to 1600 and 1535 cm^{-1}, respectively in case of the complexes. This shows that there is coordination through N atom of the deprotonated amide group of the glycylglycine[17]. It is also observed that there is shift in the asymmetric and symmetric streching frequencies of the carboxylate group of amino-acids and follows Nakamoto's order[18] (asymmetric streching frequencies increase while symmetric streching frequencies decrease due to coordination), indicating that there is coordination through carboxylate group of the amino acids. Two new bands appear for all the complexes at 435 and 535 cm^{-1} which may be due to Cu-O bond[19] and C-N bond[19], respectively. The difference in asymmetric and symmetric streching frequencies of the carboxylate group provides a clue that Cu-O bond is ionic[20] in nature.

Electronic spectra : All the complexes give a single asymmetric absorption band at ~16000 cm^{-1} (ϵ=~200), which shows that these complexes are of tetragonally distorted octahedral geometry[11,21].

Polarographic investigations : Electroreduction of the complexes investigated is found to be a single step, two electron, irreversible reduction at the dropping mercury electrode (dme). The values of $i_d/\sqrt{h_{corr}}$ for all the complexes under study are almost constant for three different heights of the mercury column. This confirms that the limiting current for all the processes of electroreduction are diffusion-controlled.

The slopes of the plot of -E *vs* log $(i_d-i)/i$ for the current potential curves have been used as a criterion for reversibility. Slope values observed for all the complexes are found to be greater than the theoretical values at all the temperature and thus exhibiting that the process of electroreduction is irreversible. The transfer coefficient, α, and the half wave potential, $E_{\frac{1}{2}}$, have been determined from Oldham and Parry's method[22]. For the comparison of the rate of electron transfer of all the complexes, rate constant, K_r has been calculated at −0.30 V against SCE, which is more useful than comparison of rate constants at formal potentials[23], using the following equation

$$E_{\frac{1}{2}}=E_r+\frac{2.303\ RT}{\alpha\ nF}\log 0.89\ Kr\sqrt{t/D}$$

TABLE 2—POLAROGRAPHIC CHARACTERISTICS OF MIXED LIGAND COMPLEXES OF COPPER(II)-GLYCYLGLYCINE AND SOME AMINO-ACIDS IN AQUEOUS 0.1 *M* SODIUM PERCHLORATE MEDIUM

h_{corr} = 58.5 cm, [Depolariser] = 10^{-3} *M*, [Triton X-100] = 0.001 %

Complex no.	Temp. °C	i_d μA	$-E_{\frac{1}{2}}$ V	Slope V	α	$D^{\frac{1}{2}} \times 10^3$ cm²sec⁻¹	$k_r \times 10^3$ cm sec⁻¹	Q_D k cal mol⁻¹
I	25	8.23	0.278	0.20	0.15	4.14	3.07	3.8
	35	9.22	0.275	0.23	0.14	4.64	3.48	
	45	10.35	0.274	0.24	0.13	5.21	3.89	
	55	10.69	0.269	0.25	0.13	5.39	4.23	
II	25	9.05	0.276	0.22	0.14	4.50	3.38	3.5
	35	9.61	0.272	0.22	0.14	4.84	3.77	
	45	10.64	0.269	0.25	0.13	5.36	4.22	
	55	11.84	0.264	0.27	0.12	5.96	4.82	
III	25	9.26	0.290	0.22	0.14	4.61	2.96	3.6
	35	10.29	0.284	0.24	0.12	5.18	3.49	
	45	11.00	0.282	0.26	0.12	5.54	3.75	
	55	11.79	0.275	0.27	0.12	5.93	4.32	
IV	25	7.88	0.272	0.24	0.12	3.97	3.00	3.5
	35	8.85	0.270	0.22	0.14	4.47	3.55	
	45	9.77	0.269	0.28	0.11	4.88	3.76	
	55	10.42	0.267	0.28	0.11	5.27	4.11	
V	25	8.16	0.257	0.21	0.14	4.11	3.75	3.4
	35	9.58	0.256	0.24	0.13	4.82	4.29	
	45	10.72	0.255	0.26	0.12	5.40	4.73	
	55	11.43	0.247	0.26	0.12	5.75	5.58	

where all the terms have their usual significance.

The values of i_d, at different temperatures have been used to calculate the activation energy of diffusion, Q_D, by Vlček's equation [24]

$$\log \frac{i_d}{m^{2/3}t^{1/6}} = \log 0.627\ nFCD^{\frac{1}{2}} - \frac{1/2\ Q_D}{2.3\ RT}$$

The polarographic characteristics of all the complexes at different temperatures have been given in Table 2. The perusal of the results shows that the values of i_d increase with the rise in temperature for all the complexes, which may be due to the increased concentration of the depolariser at the electrode surface with increasing temperature. For all the complexes $E_{\frac{1}{2}}$ goes on decreasing, *i.e.* shifts towards more positive potential, with the rise of temperature, showing easier reduction may be attributed to (a) the increase of energy of the electrons in the electrode, which will reach fermi level[25] easily, and (b) the easier availability[26] of the vacant orbital in the depolariser. The graph plotted temp. *vs* $E_{\frac{1}{2}}$ for the complexes I, II and IV is a straight line showing that the mechanism[28] of electroreduction for these complexes do not change with temperature, while for complexes III and V these plots are nonlinear, which indicates that the mechanism[28] of electroreduction for these two complexes varies with temperature.

For the sake of comparison of polarographic behaviour with spectral behaviour, the polarographic characteristics ($E_{\frac{1}{2}}$, K_r) and the corresponding spectral parameter, ν_{max}, are given in Table 3. On the basis of ν_{max} values the strength of the ligands should be in the order

thr > alan > gly ~ ser ~ val

TABLE 3—SPECTRAL AND POLAROGRAPHIC PARAMETERS OF THE MIXED LIGAND COMPLEXES OF COPPER(II) WITH GLYCYLGLYCINE AND SOME AMINO-ACIDS AT 25±0.2°

Complex no.	$-E_{\frac{1}{2}}$ V	$K_r \times 10^3$ cm sec⁻¹	ν_{max} cm⁻¹
I	0.278	3.07	15870
II	0.276	3.38	15820
III	0.290	2.96	15750
IV	0.272	3.00	15750
V	0.257	3.75	15750

Hence, one would expect that the values of half wave potential should be in the order[8,26]

thr > alan > gly ~ ser ~ val

provided no non-structural factor plays any part. But the perusal of Table 3 reveals that the electroreduction of III is the most difficult one. These anomalous observations may be rationalized by assuming that each of the complex orients at the electrode surface such that the (gg) ligand lies away from the electrode and the other ligand lies towards the electrode surface. On the basis of the steric effects, one would expect the values of the half wave potential to be in the order

val > thr > alan > ser > gly

Table 3 shows that this order is obeyed by all the complexes except glycine complex as the $E_{\frac{1}{2}}$ for complex IV is greater than that for V. The

electrocapillary curves for these complexes show that only the complex of serine and that of glycine adsorb at the electrode surface, which leads to the conclusion that the $E_{\frac{1}{2}}$ of these two complexes should decrease, but it does not give any hint as to why serine complex is reduced easily. Most probably, the presence of $-OH$ group in the serine ligand makes the reduction easier due to its electron withdrawing nature.

This observation can be further rationalized by considering a proper symmetry of the depolariser and its orientation at the electrode surface. As has been reported earlier[11] and on the basis of ν_{max} and ϵ values, these complexes are of tetragonally distorted octahedral geometry, hence the local symmetry of copper(II) ion in the solution may be assumed to be D_{4h}. In this symmetry, the splitting of the five d orbitals of copper(II) ion is such that the energy of the orbitals is in the order

$$d_{xz}, d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$$

Therefore the accommodation of nine electrons in different 3d orbitals would be as follows

$$(d_{xz})^2 (d_{yz})^2 (d_{z^2})^2 (d_{xy})^2 (d_{x^2-y^2})^1$$

Considering that the orientation of the complex particle is such that the xz plane (or yz plane) is perpendicular to the electrode surface, the d_{z^2} and also the d_{xz} (or d_{yz}) orbital point towards the electrode. The two incoming electrons needed for electroreduction should be accommodated in the lowest lying vacant orbital, $d_{x^2-y^2}$ in the present case. But this orbital is incapable of receiving the electrons due to its very low electron affinity and unfavourable orientation. Out of the two suitably oriented orbitals, namely d_{z^2} and d_{xz} (or d_{yz}), the later is low lying and hence it must be vacated prior to the electron transfer proper. The two electrons of this orbital are promoted under the strong influence of the electrode field to the next higher vacant orbitals, thus enabling d_{xz} (or d_{yz}) orbital to function as redox orbital. The promotion energy required for this process would depend upon the energy difference between the non-bonding e_g (d_{xz}, d_{yz}) orbitals and the anti-bonding b_{1g*} and a_{1g*} orbitals, which also depend on the ligand field strength and hence the case of electroreduction of the depolariser may be correlated with ligand field strength as has been observed (Table 3).

Acknowledgement

Two of the authors (S.N.M. and P.K.C.) are thankful to the U.G.C., New Delhi for the award of Teacher Research Fellowship.

References

1. V. SRIVASTAVA, K. B. LAL and H. L. NIGAM, *J. Indian Chem. Soc.*, 1982, **59**, 497.
2. D. BANERJEA and P. BANERJEA, *J. Indian Chem. Soc.*, 1972, 49, 1321.
3. A. A. VLČEK, *Rev. Chim. Miner.*, 1968, **15**, 299.
4. J. MASEK, *Inorg. Chim. Acta Rev.*, 1969, **3**, 99.
5. H. S. SHARMA and H. L. NIGAM, *Indian J. Chem., Sect. A*, 1976, **14**, 410.
6. A. A. VLČEK, *Electrochim. Acta*, 1968, **13**, 1063.
7. G. SHIVON, S. ZEECHIN and G. PILLONI, *J. Inorg. Nucl. Chem.*, 1977, **39**, 115.
8. S. N. MANDLOI, P. K. CHITALE and M. S. VERMA, *Vijnan Parishad Anusandhan Patrika*, 1982, **25**, 389.
9. M. S. BALKRISHNAN, P. NATARAJAN and M. SANTAPPA, *Curr. Sci.*, 1975, **44**, 303.
10. R. P. MARTIN and L. MOSSONI, *J. Biol. Chem.*, **1971**, **246**, 5944.
11. I. NAGYPAL and A. GERGELY, *J. Chem. Soc., Dalton Trans.*, 1977, 1109.
12. H. SIGEL, *Inorg. Chem.*, 1975, **14**, 1535.
13. E. W. HUGHES and W. J. MOORE, *J. Am. Chem. Soc.*, 1949, **71**, 2618.
14. H. W. THOMPSON, D. L. NICHOLSON and L. N. SHORT, *Faraday Discuss. Chem. Soc.*, 1950, **9**, 222.
15. R. J. KOGEL, J. P. GREENSTEIN, M. WINITZ, S. M. BIRNBAUM and R. A. MCCALLUM, *J. Am. Chem. Soc.*, 1955, **77**, 5708.
16. J. A. KIEFF and K. NAKAMOTO, *J. Inorg. Nucl. Chem.*, 1961, **292**, 2561.
17. M. K. KIM and A. E. MARTEEL, *Biochemistry*, **1964**, **3**, 1169.
18. K. NAKAMOTO, *J. Am. Chem. Soc.*, 1963, **83**, 4528.
19. C. R. SAXENA, Ph.D. Thesis, Vikram University, **1978**.
20. D. SAWYER and P. PAULSON, *J. Am. Chem. Soc.*, **1958**, **88**, 1597.
21. N. S. GILL and R. S. NYHOLM, *J. Chem. Soc.*, **1959**, 1977.
22. K. B. OLDHAM and E. P. PARRY, *Anal. Chem.*, **1968**, **40**, 65.
23. A. A. VLČEK, *Prog. Inorg. Chem.*, 1965, **5**, 211.
24. A. A. VLČEK, *Collect. Czech. Chem. Commun.*, **1959**, **24**, 3538.
25. J. O'M, BOKRIS, *J. Chem. Educt.*, 1971, **48**, 352.
26. S. S. SINGH, M. S. VERMA and H. L. NIGAM, *Electrochim. Acta*, 1978, **23**, 1287.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 590-592

Thermodynamics of Complex Formation between Neodymium(III) and Carboxymethylthiosuccinic Acid and Equilibrium Study of Mixed Complexes with Simple and Substituted Dicarboxylic Acids

D. N. SHELKE

Department of Chemistry, Marathwada University, Aurangabad-431 004

Manuscript received 25 October 1983, accepted 17 June 1984

Complexing of neodymium ion with carboxymethylthiosuccinic and dicarboxylic acids have been studied in aqueous solution potentiometrically and the relevant stability constants have been evaluated using computer technique. Carboxymethylthiosuccinic acid has been shown to form 1 : 2 complexes more readily than other dicarboxylic acids. The thermodynamics of the complex formation have been evaluated by potentiometric equilibrium data and the relationship between the site of coordination. and the thermodynamic quantities has been discussed. The results of mixed complexes are explained in terms of substituent influences upon the chelation of malonic and succinic dianions to Nd^{III}-CMTSA systems and the relationship between stabilization parameter ($\triangle$logK) and the ligand basicity.

THE pronounced biological activity[1,2] of the metal complexes of ligands derived from thio acids has led to interest in their coordination chemistry. However, studies made so far deal exclusively with the stereochemistry of transition metal complexes[3,4] and the coordination behaviour of these ligands with organometallic moieties[5,6]. Our continuing interest in chelated Cu^{II} and Nd^{III} complexes has led us to suggest the tridentate and bidentate nature of thiodiacetic acid[7,8] and to study their stereochemistry along with their biological activity.

We report here, in addition to few data for binary complexes already reported[9] the equilibrium studies on the mixed-ligand complex formation occuring when neodymium(III) is mixed with carboxymethylthiosuccinic and dicarboxylic acids. Special consideration was made for the investigation of the substituent effects as favouring the unsymmetrical rather than the symmetrical dimethyl derivatives[10].

Experimental

The dicarboxylic acids such as succinic, itaconic, chlorosuccinic, methylmalonic, dimethylmalonic, ethylmalonic, diethylmalonic, thiodiacetic and 3,3'-thiodipropionic were of Fluka and AnalaR grade. Carboxymethylthiosuccinic acid (CMTSA) was of AnalaR quality. Neodymium nitrate (AnalaR) was used and its concentration was estimated as Nd_2O_3. All solutions were prepared in conductivity-water (pH = 6.8, conductivity = 1.6×10^{-6} Ω^{-1}). The details of other chemicals are described in our earlier reports[11-13].

Neodymium complex formation constants were calculated from potentiometric titration curves of the carboxymethylthiosuccinic and dicarboxylic acids in absence and presence of neodymium. Changes in pH were followed using glass and calomel electrodes, and Elico LI-10 digital pH meter. All investigations were carried out under nitrogen atmosphere at 30° and ionic strength 0.1 mol dm^{-3} ($NaClO_4$). From the calculation of the formation constants a Fortran computer programme was used for the evaluation of equilibrium constants and the concentrations of the species present in the ternary complex. All computations were made at Tata Institute of Fundamental Research, Bombay.

Results and Discussion

The results of the equilibrium studies are summarized in Table 1 in addition to the few data for binary complexes already reported. In the present work, stability constant values are comparable with those reported in the literature and the values differ at different experimental conditions. The standard deviation of the data for the equilibrium constants of binary and ternary complexes was ±0.05 log units. A representative data, *i.e.* Nd^{III} carboxymethylthiosuccinic-thiodipropionic acid system explain adequately the precision of the experimental work (Table 2).

We have previously elucidated the binding properties of carboxymethylthiosuccinic acid with lanthanides, particularly neodymium ion, employing the equilibrium constant data, thermodynamic parameters and also the electrostatic and cratic

TABLE 1—PROTON AND NEODYMIUM COMPLEX FORMATION CONSTANTS FOR CARBOXYMETHYLTHIOSUCCINIC ACID (CMTSA) AND DERIVED THERMODYNAMIC PARAMETERS

Temp. 30°, μ = 0.1 mol dm^{-3}

Constants	pK/log K	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	$-\Delta S$ JK^{-1} mol^{-1}
pK_1	2.91 2.80[a]	16.91 (4)	5.27 (12)	9.2 (4)
pK_2	3.91 3.90[a] 3.79[b]	22.69 (3)	3.51 (14)	15.1 (7)
pK_3	5.03 5.05[a]	29.21 (3)	3.52 (15)	20.3 (9)
log K_1^o	4.10	−23.79	−4.37	+92.9
log K_2^o	3.25	−18.86	−6.13	+82.4

Standard deviation in parentheses.
[a]Ref. 28, [b]Ref. 29, [c]Ref. 15.

TABLE 2—EQUILIBRIUM CONSTANT FOR THE NEODYMIUM(III)-CARBOXYMETHYLTHIOSUCCINIC ACID (CMTSA) (Y)-THIODIPROPIONIC ACID (X) SYSTEM

Temp. = 30°, μ = 0.1 mol dm^{-3}

pH	$[H^+] \times 10^5$	K^M_{MXY}	K_{DXY}	K^{MX}_{MXY}	K^{MY}_{MYX}
4.35	5.372	7.773	1 313	3 673	4.563
4.45	4.267	7.797	1.337	3.697	4.587
4.60	3.020	7.773	1.313	3.673	4.563
4.70	2.399	7.759	1.299	3.659	4.549
4.80	1.905	7.763	1.309	3.669	4,559
4.85	1.698	7.760	1.300	3.660	4.550
4.90	1.513	7.763	1.303	3.663	4.553
4.95	1.349	7.777	1.317	3.677	4.567
Average		7.7(8	1.307	3.667	4.557

components of these thermodynamic parameters[14,15]. The formation of Nd^{III}-CMTSA complexes is enthalpically disfavoured but entropically favoured. This indicates that the metal ion is bound to oxygen of the carboxylate groups of carboxymethylthiosuccinic acid. The contribution to the total enthalpy by the carboxylate group in complexation was apparently either very small or probably slightly endothermic, suggesting that no information of the metal ion with sulphur donor atoms is present in neodymium complexes. This explanation of the thermodynamic data is in agreement with that previously suggested[16,17], and very recent report[18,19] for mixed-ligand complexes. The stability constants obtained for methyl and ethyl malonic acids are expected on the basis of nature of substituent in the parent malonic except in dimethylmalonic acid.

To extend the complexity of the system as a means of characterising by electronic and ir spectra as spectroscopic probe have been investigated. It has been observed that there is no interaction between sulphur atom and neodymium ion. Further, the prepared solid complex is paramagnetic, giving Bhor Magneton values corresponding to one unpaired electrons. These detailed studies will be reported in a forthcoming publication.

The stabilization constant of the complex stability (Δ log K) is the difference between measured values of stability constants which is defined[20] as

$$\Delta \log K = \log K^{MX}_{MXY} - \log K^{M}_{MY}$$
$$= \log K^{MY}_{MYX} - \log K^{M}_{MX} \quad (1)$$

The disproportionation constant (K_{DXY}) can be given by reaction (2)

$$MX_2 + MY_2 \rightleftharpoons 2\ MXY \quad (2)$$
$$K_{DXY} = 2 \log K^{M}_{MXY} - (\log K^{M}_{MX_2} + \log K^{M}_{MY_2})$$

The complex stability is a measure of the affinity that secondary acid has bonding to the aquated metal ion and to the complexes Nd^{III}-CMTSA. Since more coordinating sites are available for bonding the first ligand to a metal ion than for the second ligand, ΔlogK should, in general be negative[21]. In aqueous solution neodymium ion[22] is present as $[Nd(H_2O)_9]^{3+}$, $[Nd(H_2O)_8]^{3+}$ and $[Nd(H_2O)_6]^{3+}$. The metal chelate is formed due to the simultaneous replacement of water molecules from the coordination sphere of neodymium ion with the formation of Nd-O bonds. Thus the values of ΔlogK and K_{DXY} would be −0.6 and 0.6, respectively, values markedly greater than these suggesting the preferential formation of mixed-ligand complexes than binary ones. However, the value of K_{DXY} is clearly dependent on the stabilities of the simple binary bis-complexes.

Table 3 summarizes the formation constants for the binary bis- and mixed-ligand complexes of neodymium ion and the following important points for the formation of mixed complexes may be noticed from the tabulated data.

(a) The values of ΔlogK are negative, pointing to the preferential formation of ternary complexes than binary ones. However, in case of Nd^{III}-CMTSA-thiodipropionic acid system, ΔlogK is positive, which qualifies the positions of the equilibrium[23,24] $MX + MY \rightleftharpoons MXY + M$. Despite of low ΔlogK (−0.14) in chlorosuccinic acid system, the sufficient stability of the mixed-ligand complex is due to the favourable value of K_{DXY}.

(b) Significantly greater values of K_{DXY} than 0.60 expected from statistical considerations except in succinic and intaconic acid systems, demonstrate the stabilized nature of mixed-ligand complexes.

(c) The values of $\log K^{MX}_{MXY}$ and $\log K^{MY}_{MY_2}$ show the preferential formation of ternary complexes. A comparison of $\log K^{MY}_{MYX}$ with $\log K^{MX}_{MX_2}$ values, especially in the systems involving methyl and ethyl substituted malonic acids, reveals the

TABLE 3—FORMATION CONSTANTS FOR TERNARY COMPLEXES OF NEODYMIUM(III)-CARBOXYMETHYLTHIOSUCCINIC (CMTSA)-DICARBOXYLIC ACIDS

Temp.30°, μ = 0.1 mol dm^{-3} ($NaClO_4$)

Acids	log K^{M}_{MXY}	K_{DXY}	K^{MX}_{MXY}	K^{MY}_{MYX}	K^{M}_{MX}	$K^{MX}_{MX_2}$	Δ log K
Succinic	6.76 (4)	0.13	2.64	3.40	3.38[a]	–	−0.72
Itaconic	7.03 (3)	0.01	2.93	3.26	3.77[a]	–	−0.84
Chlorosuccinic	6.38 (3)	0.71	2.28	3.96	2.42 (2)	–	−0.14
Methylmalonic	8.85 (2)	2.11	4.75	3.52	5.33 (2)	2.91 (1)	−0.58
Dimethylmalonic	8.58 (4)	2.18	4.48	3.63	4.95 (3)	2.68 (2)	−0.47
Ethylmalonic	8.56 (3)	1.83	4.46	3.46	5.10 (2)	2.84 (3)	−0.64
Diethylmalonic	8.61 (2)	2.01	4.51	3.49	5.12 (1)	2.71 (4)	−0.71
Thiodiacetic	7.08 (2)	0.61	2.98	3.86	3.22[b]	–	−0.24
3,3′-thiodipropionic	7.77 (1)	1.31	3.67	4.56	3.21[b]	–	+0.46

Standard deviations are given in parentheses.

[a]Ref. 9, [b]Ref. 30.

preferential formation of mixed complexes than binary bis ones.

(d) The experimental data was utilized to plot the complex stability against the ligand basicity[25,26]. A straight line relationship of positive slope was observed. Because of its double bond character, itaconic acid is deviated from the expected straight line, indicating the extra stabilization. As a part of systematic study of mixed-ligand complexes of Be^{II}, we discussed this interesting aspect of double bond character in maleic acid and explained on the basis of π electron distribution[27].

(e) It is clearly seen from the tabulated values of K^{M}_{MXY} and the stabilization parameters ΔlogK and K_{DXY} that the inductive effect of the substituent group has no great influence on the stability of these complexes, except in dimethylmalonic acid system. The presence of the two bulky substituents as in the case of Nd^{III}-CMTSA-diethylmalonic acid system seems especially to favour the formation of ternary species, probably by forcing the two carboxylate groups into the best position of chelation.

Acknowledgement

The author is indebted to Prof. S. S. Pawar for his keen interest, to Dr. L. G. Pardeshi for helpful discussions, and to T.I.F.R. computer centre for generous allotment of computer time. The work is supported by U.G.C., New Delhi.

References

1. S. E. LIVINGSTONE and M. DAS, *Brit. J. Cancer*, 1978, **37**, 466.
2. M. DAS and S. E. LIVINGSTONE, *Inorg. Chim. Acta*, 1976, **5**, 19.
3. F. CASSASSAS, L. ARIAS, J. JUAN and F. GARCIA-MONTELONGO, *J. Chim. Phys. Chim. Biol.*, 1977, **74**, 324.
4. M. A. ALI, S. E. LIVINGSTONE and D. J. PHILIPS, *Inorg. Chim. Acta*, 1973, **7**, 179.
5. G. DOMAZETIS, R. J. MAGEE and D. B. JAMES, *J. Organomet. Chem.*, 1979, **173**, 357.
6. R. P. BONOMO, E. RIZZARELLI, N. BRESCIANI-PAHOR and G. MARDIN, *J. Chem. Soc., Dalton Trans.*, 1982, 681.
7. D. N. SHELKE, *Inorg. Chim. Acta*, 1979, **32**, L45.
8. D. N. SHELKE, *J. Indian Chem. Soc.*, in the press.
9. D. N. SHELKE and D. V. JAHAGIRDAR, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2142.
10. D. N. SHELKE, *J. Chem. Res. (S)*, 1983, 92 ; *J. Chem. Res. (M)*, 1983, 828.
11. D. N. SHELKE, *J. Coord. Chem.*, 1982, **12**, 35.
12. D. N. SHELKE, *Inorg. Chim. Acta*, 1983, **80**, 255.
13. D. N. SHELKE, *J. Indian Chem. Soc.*, 1982, **59**, 833.
14. D. N. SHELKE, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1653.
15. D. N. SHELKE, B. R. ARBAD and D. V. JAHAGIRDAR, *Indian J. Chem., Sect. A*, 1983, **22**, 124.
16. A. E. MARTELL, *Recl. Trav. Chim. Pays*, 1956, **75**, 781.
17. G. R. CHOPPIN and J. A. CHOPPORIAN, *J. Inorg. Nucl. Chem.*, 1961, **22**, 97.
18. G. ARENA, R. CALI, V. CUCINOTTA, S. MUSUMECI, E. RIZZARELLI and S. SAMMARTANO, *J. Chem. Soc., Dalton Trans.*, 1983, 1271.
19. G. ARENA, R. P. BONOMO, S. MUSUMECI, R. PURRELLO, E. RIZZARELLI and S. SAMMARTANO, *J. Chem. Soc., Dalton Trans.*, 1983, 1279.
20. H. SIGEL, *Angew Chem.*, 1975, **14**, 394.
21. G. BROOKES and L. D. PETTIT, *J. Chem. Soc., Dalton Trans.*, 1977, 1918.
22. T. MOELLER, "Comprehensive Inorganic Chemistry", Pergamon Press, Oxford, 1973, p. 4, 1.
23. H. SIGEL, "Metal Ions in Biological Systems", Marcel Dekker, New York, 1973, pp. 2, 65.
24. D. N. SHELKE and D. V. JAHAGIRDAR, *J. Inorg. Nucl. Chem.*, 1979, **41**, 925, 929, 1635.
25. H. SIGEL, *J. Inorg. Nucl. Chem.*, 1975, **37**, 507.
26. H. SIGEL, R. CARACO and B. PRIJS, *Inorg. Chem.*, 1974, **13**, 462.
27. D. N. SHELKE, *J. Indian Chem. Soc.*, 1983, **60**, 631.
28. K. P. DUBEY and M. K. Puri, *Rev. Chim. Minor*, 1975, **12**, 255.
29. V. CERDA, F. CASSASSAS and F. GARCIA-MONTELONGO, *Thermochim. Acta*, 1981, **47**, 343.
30. D. N. SHELKE and D. V. JAHAGIRDAR, *J. Indian Chem. Soc.*, 1979, **56**, 344.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 593-594

Stability Constants of Complexes of 7-Dicyclohexylamino-methyl-8-hydroxyquinoline with Copper(II), Nickel(II), Cobalt(II) and Manganese(II)

KAMAL K. CHATURVEDI* and (Miss) M. GOYAL

Department of Chemistry, Holkar Science College, Indore

Manuscript received 26 December 1983, accepted 17 June 1984

The stability constants of 7-dicyclohexylaminomethyl-8-hydroxyquinoline complexes of Cu^{II}, Ni^{II}, Co^{II} and Mn^{II} were determined potentiometrically in 3 : 1 (v/v) dioxane-water mixture at ionic strength $\mu = 0.1$. The successive formation constants log K_1 and log K_2 were determined employing Irving-Rossotti method. The order of stability constants is $Cu^{II} > Ni^{II} > Co^{II} > Mn^{II}$, which is in accordance with Irving-Williams rule.

POTENTIOMETRIC studies have been carried out on metal complexes of Cu^{II}, Ni^{II}, Co^{II} and Mn^{II} with 7-dicyclohexylaminomethyl-8-hydroxyquinoline. The dissociation constants of the ligand and formation constants of its metal complexes have been determined by modified Bjerrum's method at 25±0.1° in 3 : 1 (v/v) dioxane-water medium. The ionic strength was maintained at 0.1 μ by the addition of $NaClO_4$.

Experimental

The ligand 7-dicyclohexylaminomethyl-8-hydroxyquinoline was prepared by adding formaldehyde to dicyclohexylamine (0.02 mol each) with constant shaking. The mixture was allowed to cool for 15 min and then added 8-hydroxyquinoline (0.02 mol) in 20 ml ethanol. After adding a drop of conc. HCl, the mixture was refluxed for 45 min at 70-80° with constant stirring. The reaction mixture was allowed to stand for a day. The solid obtained was then separated and crystallized in solvent ether and dried to yield yellowish brown product, m.p. 135-140°. The purity of the ligand was further confirmed by tlc.

The dioxane used was purified by the standard method[1]. Double distilled water was used throughout the experiment. The ligand solution was prepared in purified dioxane. Metal solutions were prepared in perchloric acid and the solutions of $HClO_4$ and $NaClO_4$ in double distilled water.

*p*H values were recorded employing Philips PP 9045 digital *p*H meter. For *p*H measurements following sets of solutions were prepared and titrated against standard carbonate free sodium hydroxide solution (0.5 *M*) in an atmosphere of nitrogen.

(a) 5 ml (0.1*M*) $HClO_4$ + 5 ml (0.70*M*) $NaClO_4$ + 30 ml dioxane.

(b) 5 ml (0.1*M*) $HClO_4$ + 5 ml (0.70*M*) $NaClO_4$ + 5 ml (0.05 *M*) ligand + 25 ml dioxane.

(c) 2.5 ml (0.1 *M*) $HClO_4$ + 2.5 ml (0.01*M*) metal solution in (0.1*M*) $HClO_4$ + 5 ml (0.70*M*) $NaClO_4$ + 5 ml (0.05*M*) ligand + 25 ml dioxane.

The total volume of each system was kept at 40 ml maintaining 3 : 1 (v/v) dioxane-water medium. The appropriate correction factor for converting *p*H meter readings (B values) to $-[H^+]$ in 3 : 1 (v/v) dioxane-water was applied[2] and the curves were plotted accordingly.

The ligand did not undergo hydrolysis under the experimental conditions as indicated by the rapid attainment of equilibrium during the titrations and by the absence of any significant drift in *p*H even after 2 h.

Results and Discussion

From the titration curves of solutions (a) and (b) $\bar{n}_A$ values at various B values were calculated and plotted against B using the formula of Irving and Rossotti[3]. The values of pK_1^H and pK_2^H were evaluated from half-integral points at $\bar{n}_A = 0.5$ and 1.5, respectively. The values so obtained were further corroborated by the straight line plots of log $[\bar{n}_A/1-\bar{n}_A]$ *vs* B, and log $[(2-\bar{n}_A)/\bar{n}_A-1]$ *vs* B, respectively.

From the titration curves of solutions (b) and (c), $\bar{n}$ and *p*L values were calculated. Metal ligand formation curves (Fig. 1) obtained by plotting $\bar{n}$ against *p*L were utilized to calculate successive stability constants of metal complexes using Rossotti's computational techniques[4]. The formation curves for Cu^{II} and Ni^{II} are complete at

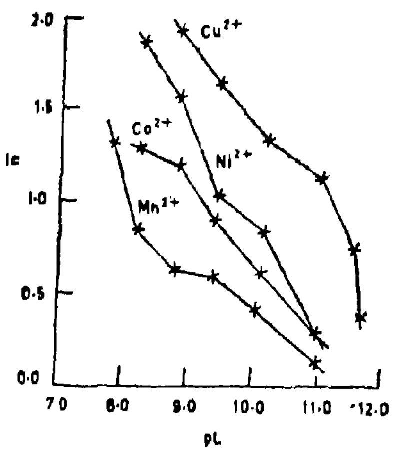


Fig. 1. Metal ligand formation curves.

both the ends, hence values of log K_1 and log K_2 were obtained by (i) interpolating at $\bar{n}=0.5$ and 1.5, respectively (half integration method), (ii) least square method, (iii) mid point method. The formation curves for Co^{II} and Mn^{II} are however incomplete in upper half portion due to the occurrence of precipitates and hence log K_1 is calculated by half integration and mid point methods, and log K_2 by mid point method using the equation

$$\log K_1 . K_2 = 2pL \quad (\text{at } \bar{n}=1.0).$$

The calculated values of log K_1 and log K_2 along with the protonation constants of the ligand have been reported in Table 1. The results indicate that the stability of the different complexes investigated follow the order $Cu^{II} > Ni^{II} > Co^{II} > Mn^{II}$, which is in accordance with Irving-Williams rule[4].

TABLE 1—STABILITY CONSTANTS OF METAL COMPLEXES OF 7-DICYCLOHEXYLAMINOMETHYL-8-HYDROXYQUINOLINE

Temp. = 25°, μ = 0.1

	H^+	Cu^{II}	Ni^{II}	Co^{II}	Mn^{II}
log K_1	11.45	a 11.70	10.65	10.42	10.0
		b 11.596	10.62	–	–
		c 11.70	10.65	10.42	10.0
log K_2	4.3	a 9.75	8.9	–	–
		b 9.963	9.490	–	–
		c 10.32	9.05	7.78	6.14

a = Half integration method, b = Least square method, c = Mid point method.

Acknowledgement

The authors wish to thank University of Indore, for the award of J.R.F. to (M G.).

References

1. A. I VOGEL, "A Text Book of Practical Organic Chemistry", 3rd. ed. Longmans, London, 1959, p.177.
2. H. M. N. H. IRVING and U. S. MANHOT, *J. Inorg. Nucl. Chem.*, 1968, 30, 1215.
3. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397 ; 1954, 2904.
4. H. IRVING and R. J.P. WILLIAMS, *Nature (London)*, 1948, 162, 746.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 595-597

Study of Formation Constants of Substituted Salicylanils and 2'-Hydroxysalicylanils

S. S. DODWAD*, (Mrs.) INDIRA PATIL and M. G. DATAR

Physical Chemistry Laboratory, The Institute of Science, 15, Madam Cama Road, Bombay-400 032

Manuscript received 12 February 1983, revised 9 March 1984, accepted 17 June 1984

The proton-ligand stability constants of some substituted salicylanils and 2'-hydroxysalicylanils have been studied by the Bjerrum-Calvin *p*H titration technique in water-dioxane medium (1 : 3 v/v) at $\mu \sim 0.1$ ($NaClO_4$) and at 30° (±0.1). The results have been discussed on the basis of the electromeric effects of substituent groups with regard to their nature and position in the salicylaldehyde and aniline nucleus.

The proton-ligand stability constants for closely related substituted anils are found to vary in the following order in terms of their substituents.

2'-CH_3 < 3'-CH_3 < 4'-CH_3 and similarly 2'-chloro < 3'-chloro < 4'-chloro and further as propiophenone < acetophenone.

SCHIFF bases derived from the condensation reaction of aromatic aldehydes with aliphatic and aromatic amines represent an important series of widely studied ligands[1-4]. In the present investigation the authors have undertaken the study of formation constants of a series of fourteen closely related Schiff-base ligands obtained by the reaction of different aldehydes with a number of amines to explore the equilibria which exists when the metal ions interact with these ligands in solution.

Experimental

All chemicals and reagents used in the study were either A.R. grade or purified by conventional methods before use.

Preparation of chelating ligands: Salicylanils and 2'-hydroxysalicylanils were prepared by following the reported method[5]. Compound nos. 3 to 8 were prepared by condensing salicylaldehyde and corresponding amine, compound nos. 9 to 12 by condensing 2-hydroxyacetophenone and 2-hydroxypropiophenone with aniline and *o*-aminophenol, and compound nos. 13 and 14 by condensing resorcyldehyde and benzaldehyde with *o*-aminophenol. The compounds were recrystallised from methanol and preserved in vacuum desiccator. Their purity was ascertained by elemental analysis and checking their melting points.

Bjerrum-Calvin[6,7] *p*H-titration technique as adopted by Irving and Rossotti[8] was followed to determine proton-ligand stability constants in dioxane-water (3 : 1, v/v) medium at constant temperature 30° (±0.1°) and in presence of 0.8*M* sodium perchlorate to maintain constant ionic strength ($\mu \sim 0.1$).

Results and Discussion

The relation in dioxane-water medium was reported[9] in mixtures of different compositions to follow the equation

$$-\log (H) = B + \log f + \log U^{\circ}H \qquad (1)$$

where $U^{\circ}H$ is a correction factor. This correction factor for *p*H was used by Bjerrum in his "formation function" for $\bar{n}_A$ which on simplification expressed as

$$\bar{n}_A = y - \frac{(V''-V')}{(V^{\circ}+V')} \cdot \frac{(N+E^{\circ})}{C_L^{\circ}} \qquad (2)$$

All the terms involved in the equation have their usual significance and y was taken unity.

Proton-ligand constants corresponding to acid dissociation: All the ligands studied in this investigation are involved in the formation of single complexes like LH. The formation function for such 1 : 1 complexes is given by the equation

$$\bar{n}_A + (\bar{n}_A - 1)\, pK_1^H \, 1/(\text{anti} \log B) = 0 \qquad (3)$$

This relation suggests that $\log \bar{n}_A/(1-\bar{n}_A)$ *vs* B should be linear. Such plots served to indicate the validity of $\bar{n}_A \sim B$ data and also useful to reject widely divergant data. However, the number of points that were rejected in all the cases was very small. Equation (3) may be written as

$$\log pK_1^H = B + \log \bar{n}_A/(1-\bar{n}_A) \qquad (4)$$

The practical proton-ligand stability constants were calculated by using equation (4) and are summarised in Table 1. From the plot of $\log \bar{n}_A/(1-\bar{n}_A)$ *vs* B, the graphical values of $\log pK_1^H$ were obtained as intercepts on the X-axis and reported in Table 1. According to Bjerrum the half-integral values of the formation curves are

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS

Sl. no.	Ligand	Quantity calculated	log pK^H Calcd.	log pK^H Graphical	log pK^H Half-integral	Standard deviation
1.	Salicylanil	OH d	10.45	10.45	10.46	0.202
2.	2′-Hydroxysalicylanil	OH d	9.99	10.05	10.05	0.249
3.	2′-Methylsalicylanil	OH d	10.32	10.35	10.35	–
4.	3′-Methylsalicylanil	OH d	10.38	10.40	10.40	0.200
5.	4′-Methylsalicylanil	OH d	10.76	10.80	10.80	0.225
6.	2′-Chlorosalicylanil	OH d	10.35	10.35	10.35	0.130
7.	3′-Chlorosalicylanil	OH d	10.37	10.39	10.39	0.159
8.	4′-Chlorosalicylanil	OH d	10.58	10.60	10.60	0.128
9.	2-Hydroxyacetophenoneanil	OH d	12.54	12.59	12.59	0.015
		N pa	3.18	3.16	3.15	–
10.	2′-Hydroxyacetophenone salicylanil	OH d	10.39	10.29	10.30	0.489
		N pa	3.20	3.39	3.20	0.519
11.	2-Hydroxypropiophenoneanil	OH d	12.31	12.36	12.36	0.026
		N pa	3.15	3.12	3.10	–
12.	2′-Hydroxypropiophenone salicylanil	OH d	9.98	9.98	9.98	0.232
		N pa	3.23	3.20	–	0.117
13.	4-Hydroxy-2′-hydroxysalicylanil	OH d	10.54	10.55	10.55	0.592
14.	2′-Hydroxyanil	OH d	11.42	11.50	11.45	0.369

d – dissociation ; pa – proton affinity.

equal to the formation constant, log pK^H. Graphs obtained by plotting $\bar{n}_A$ against B were wave like and the values of B at $\bar{n}_A=0.5$ are equal to log pK^H_1. The values of log pK^H_1 thus obtained by half-integral method are reported in Table 1.

Since the absorption of proton was involved in the initial stages, equation (4) is modified as

$$\log pK^H_2 = B + \log (\bar{n}_A - 1)/(2 - \bar{n}_A) \quad (5)$$

The proton affinity constant log pK^H_2 of nitrogen were calculated using this equation. Plots of $\log (\bar{n}_A - 1)/(2 - \bar{n}_A)$ *vs* B were linear and from the intercept on X-axis proton affinity constants were obtained. Half-integral value of B at $\bar{n}_A=1.5$ corresponds to proton-affinity constant of nitrogen. Such values were also obtained from proton-ligand formation curves ($\bar{n}_A \sim B$).

The values of proton-ligand stability constants calculated by the three methods reported (Table 1) reveal a close agreement. Standard deviation values calculated are also reported in Table 1. Values of log pK^H collected in the present investigation are obtained for the first time in dioxane-water (3 : 1 v/v) medium. Literature reveals that with the exception of salicylanil, work on stability constants of these ligands has not been undertaken so far. A log pK^H value of 10.44 was reported[10] for salicylanil under identical experimental conditions. It was found that this value closely agrees with the value reported.

Examination of results in Table 1 shows that log pK^H values of all the substituted 2′-hydroxy salicylanils are lower than the corresponding substituted salicylanils. The increased acid strength of these compounds must be atrributed to the presence of OH in aniline nucleus. The electronegativity of nitrogen atom due to the presence of this substituent is apparently increasing, resulting in the formation of strong hydrogen bond with the phenolic OH, which enhances the dissociation of OH. As a matter of fact-I effect of this substituent should cause a decrease in the electronic charge of nitrogen. However, the observed experimental results indicate contrary to this understanding. It is possible that in *ortho*-position+M effect of this substituent may be overcoming-I effect which might be resulting in the increased electronic charge on the nitrogen atom.

An examination of log pK^H values shows that a similar trend is noticed on *ortho*- substitution in aniline nucleus of the methyl- and chloro- groups and that the acidity of the ligands increases in the following order

$$\text{Salicylanil} < \text{-CH}_3 < \text{-Cl} < \text{-OH}$$

Further glancing of log pK^H values indicates that for isomeric substituted ligands the difference in the magnitude of log pK^H though marginal is significant and that this difference can be assigned to the substituents present in the nucleus and their position in the molecule. Discussion on log pK^H values with smaller differences in a series holds good as they are beyond experimental errors. It was reported[11] that the standard test on K<3 may be a failure in many cases of the data reported in the literature which does not necessarily mean that the complexes do not really exist or that their equilibrium constants are drastically different from the reported values. Similar is the case in the present investigation where all the general precautions[12,13] in obtaining the most correct $\bar{n}_A$ and log pK^H at each B value have been taken.

Introduction of methyl- and chloro- substituents at *meta*- position of the aniline nucleus increases the acidity of the parent ligand almost to the same extent as can be viewed from the magnitude of log pK^H values. These substituents of *meta*- position transmit electronic charge to nitrogen and hence

its electronegativity increases which results in change of acidity.

The substituted salicylanils are stabilised to a greater extent than the unsubstituted salicylanils. The order of stability runs systematically as

2′-methylsalicylanil < 3′-methylsalicylanil < 4′-methylsalicylanil and 2′-chlorosalicylanil < 3′-chlorosalicylanil < 4′-chloro salicylanil.

Further in compound nos. 9 to 12 the influence of the substituent at the double bonded carbon atom in destabilizing the phenate ion is represented by the order $H < C_2H_5 < CH_3$, the value of the reagent where only H is present as a substituent being taken from literature. In these compounds it appears that probably the inductive effect of the CH_3 and C_2H_5 groups is transmitted by the double bond in benzene to the phenolic oxygen atom thus preventing the ionisation of proton from OH and thereby preventing the formation of hydrogen bond either with ketonic oxygen or nitrogen atom as the case may be. The magnitude of log pK^H of ligand no. 12 and that of the parent ligand are almost the same. This may perphaps be attributed to the combined effect of C_2H_5 and the substituent OH in the aniline. The constant for compound no. 13 is 10.54 which is higher than the constant of parent ligand by 0.5 log units. The substituent OH in this compound is in the *meta*- position to phenolic OH. This substituent being electrophilic should decrease the electronic charge around the phenolic group and thus should cause an increase in the acid strength of the reagent. The observed value is however contrary to the expectation. The authors feel that in this case the mutual inductive effects of the OH substituents in the same benzene ring in position *meta*- with respect to each other, are acting in opposition. Besides the inductive effect, OH in aniline causes a decrease in the electronic charge around nitrogen thus weakening the N-H bond. This may be responsible for the poor dissociation of this compound. The combined effect of these substituents may be preventing the dissociation of phenolic OH.

Proton affinity of nitrogen: The values of $\bar{n}_A >$ 1 observed for all compounds studied are attributed to the presence of protonated nitrogen in the ligand. It is observed that the magnitude of proton affinity by nitrogen are almost of the same order, and that the proton affinity values of the 2′-hydroxyacetophenone salicylanil and 2′-hydroxypropiophenone salicylanil are higher than the corresponding anils. Earlier in discussion on log pK^H, it was assumed that the mesomeric effect of OH in aniline was responsible for the increased strength of N-H bond. This argument is now substantiated by the observed higher values of N-proton affinity constants of the substituted 2′-hydroxysalicylanils.

References

1. R. H. Holm, G. W. Everett and A. Chakravorty, *Prog. Inorg. Chem.*, 1966, **7**, 83.
2. L. Sacconi, *Coord. Chem. Rev.*, 1966, **1**, 126.
3. S. Yamada, *Coord. Chem. Rev.*, 1966, **1**, 415.
4. R. L. Dutta and G. P. Sengupta, *J. Indian Chem. Soc.*, 1971, **48**, 83.
5. L. Schischkoff, *Annl. Chemie*, 1957, **104**, 373.
6. J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", Haase, Copenhagen, 1941.
7. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 1945, **67**, 2003.
8. H. Irving and H. Rossotti, *J Chem. Soc.*, 1954, 2904.
9. L. G. Van Uitert and C. G. Hass, *J. Am. Chem. Soc.*, 1953, **75**, 451.
10. K. E. Jabalpurwala, B. A. Venkatachalam and M. B. Kabadi, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1011.
11. W. B. Person, *J. Am. Chem. Soc.*, 1965, **87**, 167.
12. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397.
13. J. H. Hearson and J. B. Gibert, *J. Am. Chem. Soc.*, 1955, **77**, 2594.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 598-599

Chemical Behaviour of Humic Substances at High pH
I. Titrations after End Point

M. ADHIKARI and P. SEN

Department of Agriculture, Calcutta University, 35, Ballygunge Circular Road, Calcutta-700 019

Manuscript received 16 March 1983, accepted 26 May 1984

The alkali consumption by natural and synthetic humic substances even after the complete neutralisation of acidic functional groups was investigated. Of the humic substances the excess alkali consumption after the end point was maximum in case of naturally occurring humic substances. The lower the E_4/E_6 values greater is the alkali consumption even after end point of neutralisation in acidity indicating greater aromaticity in the molecule. The presence of organically bound Fe^{3+} and Al^{3+} in a synthetic humic acid may contribute significantly to the consumption of alkali. The excess alkali required to stabilise the *p*H at 8.0 in case of synthetic humic acid prepared from glucose is due to the conversion of sugars to enols and then to its isomeric forms.

OXIDATION of humic substances under alkaline condition is an well known fact but so far little has been known about the chemical reactions in absence of oxygen[1]. It was reported[2] that excess alkali was consumed even after the complete neutralisation of the acidic groups by titration under an inert atmosphere. It was suggested that additional acidic groups were exposed due to the change in *p*H specially in the *p*H range 7.0-8.0. Humic acid with NaOH (*N*) was treated under nitrogen and oxygen atmosphere[3]. Treatment with alkali under N_2 produces some changes of humic substances like the reduction in molecular weight, small reduction in uv and visible O.D. and hydrolytic release of amino-acids. The difference in structural orientations of humic/fulvic acid with change in *p*H was observed by scanning electron microscopy[4]. The humic materials changed from fibres and bundles of fibres at low *p*H, to a finely woven net work at intermediate *p*H, and plastic type sheets and fine grains at high *p*H.

In light of the above facts, attempts have been made to compare the conformational changes on the polyelectrolyte chains of different humic substances with the addition of alkali.

Experimental

Humic acid was extracted from Mohitnagar soil by NaOH solution (0.1*N*) the by usual technique[5]. Humic acid was synthesized in laboratory from a mixture of catechol and glycine using Ca-clay (*p*H 8.2) and also in a medium containing Fe and Al oxide gels as catalysts. The humic acid synthesized using different catalysts are denoted as follows: Ca-clay (with oxide), Syn HA I; Ca-clay (without oxide), Syn HA II; Fe and All oxide gels, Syn HA III. The details of the procedure of synthesis of humic substances using clay and non-clay catalyst and synthesis of humic acid from glucose were reported earlier[6,7].

The *p*H-metric titrations were carried out with the aid of an Elico LI-10 *p*H meter. The O.D. values of samples at 465 and 665 nm were measured with an Elico CL-24 spectrophotometer. The concentration of each sample was 5 mg ml^{-1} The humic acids were adjusted at *p*H 7.0, 8.0 and 10.0 and the fulvic acid at *p*H 5.0, 7.0, 8.0 and 10.0 with NaOH (E. Merck G. R.) solution (0.01 *N*)). The *p*H values were so chosen because they covered the range at which the dissociation of acidic functional groups occur. Excess alkali was added to maintain high *p*H values when it fell more than 0.05 units. The experiments were carried out in stoppered glass bottle.

Result and Discussion

It is evident from Table 1 that for the humic acid samples, the time and quantities of alkali required to stabilise *p*H increases with increasing *p*H. The total alkali consumption in meq for stabilising *p*H in case of fulvic acid is more than any of the samples studied. Of the humic acids total alkali consumption is maximum in case of naturally occurring humic substances (Mohitnagar humic acid) than the synthetic humic acids. From the E_4/E_6 values alkali consumption for stabilising *p*H increases, *i.e.* the alkali consumption increases with the increase in aromatic character of humic acids. Humic acid prepared from glucose consumes considerable amount of alkali which might be due to the fact that sugars are considerably altered even under mild alkaline solutions. This conversion is known as Lobry, de Bruyn-Alberda, van Eckenstein transformation[8]. Alkali has one of the three following actions on sugars[8], (i) isomerization mainly at the reducing end of the sugars, (ii)

TABLE 1

Polyelectrolyte solution	*p*H	NaOH added initially meq	Time for stable *p*H h	Total NaOH consumed meq
Syn HA I	7.0	1.5×10^{-2}	16	2.5×10^{-2}
Syn HA I	8.0	2.0×10^{-2}	37	5.0×10^{-2}
Syn HA I	10.0	4.0×10^{-2}	42	1.2×10^{-1}
Syn HA II	7.0	1.2×10^{-2}	7	2.0×10^{-2}
Syn HA II	8.0	2.5×10^{-2}	22	3.2×10^{-2}
Syn HA II	10.0	3.5×10^{-2}	38	4.8×10^{-2}
Syn HA III	7.0	1.0×10^{-2}	8	2.25×10^{-2}
Syn HA III	8.0	2.6×10^{-2}	28	4.3×10^{-2}
Syn HA III	10.0	4.4×10^{-2}	45	6.8×10^{-2}
Natural HA	7.0	2.0×10^{-1}	18	2.05×10^{-1}
Natural HA	8.0	2.3×10^{-1}	52	2.4×10^{-1}
Natural HA	10.0	2.5×10^{-1}	56	2.7×10^{-1}
HA (glucose)	7.0	1.0×10^{-2}	8	2.0×10^{-2}
HA (glucose)	8.0	1.5×10^{-2}	14	2.5×10^{-2}
HA (glucose)	10.0	1.85×10^{-2}	18	2.65×10^{-2}
FA (natural)	5.0	15.15×10^{-2}	–	1.515×10^{-1}
FA (natural)	7.0	24.0×10^{-2}	14	2.5×10^{-1}
FA (natural)	8.0	25.5×10^{-2}	48	2.65×10^{-1}
FA (natural)	10.0	32.0×10^{-2}	76	3.55×10^{-1}

HA – Humic acid, FA – Fulvic acid.

fragmentation into parts having fewer carbon atoms, and (iii) internal oxidation and reduction. Enolisation is the initial step of all the above transformations.

It is also evident from Table 1 that more alkali is needed in case of synthetic humic acid HA III to attain the *p*H 10. This might be due to the presence of organically bound Fe^{3+} and Al^{3+} which may absorb hydroxyl ions to form Fe- and Al-hydroxides, similar to the results reported[9,10]. It is stated earlier that alkali consumption and time required for stabilising *p*H of natural humic substances are more than the synthetic humic acids. This higher amount of alkali consumption is mainly due to the following factors.

(a) Presence of greater molecular complexity in natural humic substances having molecular weight (M_v=28245).

(b) Presence of more dissociable acidic functional groups. From Table 2 it is noted that the E_4/E_6 value of natural humic acid is minimum, which indicates the presence of a condensed aromatic structure in it. Furthermore, the ir spectra (not shown) of the natural humic acid showed a strong absorption at 1090 cm^{-1} due to presence of cyclic aliphatic esters and alcohols. The presence of condensed aromatic network and higher amount of ester groups in the natural humic acid than the synthetic humic acids[7] may be a reason for excess alkali consumption.

TABLE 2

Sample	E_4/E_6 (*p*H 8.0)
Natural HA	0.440
Syn HA I	0.854
Syn HA II	1.425
Syn HA III	0.931
HA (glucose)	5.200

Although the E_4/E_6 values of fulvic acid is greater than most of the humic acid samples (except the humic acid from glucose), it consumes significant amount of alkali mainly due to presence of excess acidic functional groups (CEC 856 me.q/100 g). Moreover, the presence of carbohydrate molecules, mainly sugars may be a reason for excess alkali consumption because they can consume alkali to undergo chemical alterations. This is further supported from the experimental facts that humic acid prepared from glucose consumes considerable amount of alkali, though it has low molecular weight and simple molecular structure[11].

References

1. W. FLAIG, H. BEUTELSPACHER and E. REITZ, in "Chemical Composition and Physical Properties of Humic Substances in Soil Components", ed. J. E. GIESKING, Springer-Verlag, New York, 1975, Vol. 1, pp. 1-24.
2. H. DAVIS and C. J. B. MOTT, *J. Soil. Sci.*, 1981, **32**, 393.
3. R. S. SWIFT and A. M. POSNER, *J. Soil. Sci.*, 1972, **23**, 381.
4. N. SENSI, Y. CHEN and M. SCHNITZER, "Soil Organic Matter Studies", I.A.E.A., Vienna, 1977, Vol. 2.
5. M. M. KONONOVA, "Soil Organic Matter", Pergamon, Oxford, 1968.
6. M. ADHIKARI, B. MANDAL and T. K. MUKHERJEE, *Proc. Natl. Acad. Sci., India, Sect. A*, 1978, **44**, 202.
7. M. ADHIKARI, P. SEN and P. BANDHOPADHYAY, *Proc. Natl. Acad. Sci., India*, submitted for publication.
8. P. R. BLOOM, *Soil Sci. Soc. Am. Proc.*, 1979, **43**, 815.
9. P. R. BLOOM and M. B. MCBRIDE, *Soil Sci. Soc. Am. Proc.*, 1979, 43, 687.
10. R. U. LEMIEUX, in "Molecular Rearrangements", ed. P. DEMEYO, Interscience, New York, **1964**, pp. 733-35.
11. M. ADHIKARI, B. MANDAL and P. SEN, *Proc. Natl. Acad. Sci., India, Sect. A*, 1980, **46**, 387.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 600-603

Adsorption Behaviour of Anionic Dyes on Guargum Derivatives: Reclamation of Textile Effluent

R. C. KAPOOR, ADITYA PRAKASH and S. L. KALANI

Department of Chemistry, University of Jodhpur, Jodhpur-342 001

Manuscript received 17 May 1983, revised 20 March 1984, accepted 17 June 1984

The adsorption behaviour of some anionic dyes used in textile industries on newer synthesised adsorbents from guargum, namely quaternary aminised $[(CH_3)_3N^+]$, $[(C_2H_5)_3N^+]$, diethyl amino hydroxy propyl and cross-linked derivatives have been studied. Trimethyl aminised $[(CH_3)_3N^+]$ derivative was found to be a better adsorbent for the removal of color of textile effluent in both alkaline and acidic conditions. However, the most effective *p*H range was from 3 to 5. The treated effluent can be reused in the textile industry.

MANY industries in India presently discharge untreated water on land or in natural streams causing pollution of surface water, ground water and land. As a result of rapid industrialisation the water resources development schemes and water distribution systems are unable to keep pace with its increased demand. The reclamation of water for industrial reuse would minimise both these problems.

In view of the high cost and tedious procedure for the regeneration of activated carbon, there is a continuing search for low cost efficient adsorbents[1-5]. Recently we have reported the synthesis of some guargum derivatives and their applicability in the removal of colour and toxic constituents from textile waste water[6]. We, herewith, report the adsorption and desorption characteristics of some reactive, hydrolysed reactive and direct dyes on the synthesised derivatives. Such dyes are the major constituents of the colouring matter of effluents of local textile industries.

Experimental

Adsorbents: The adsorbents used in this study, namely quaternary aminised $[(CH_3)_3\overset{+}{N}]$,$[(C_2H_5)_3\overset{+}{N}]$, diethylaminohydroxypropyl and cross-linked guar were synthesised as described earlier[6].

Dyes: The following six dyes (Atul Products, India) were selected for these studies and were used as such: Procion Orange H_2R, Procion Brill Blue H_5G, Direct Red, Direct Halio-B, Procion Red M_5B (hydrolysed), Procion Blue MR (hydrolysed). The solutions of dyes were prepared freshly in distilled water. Weighted quantities of guar derivatives were contacted with aqueous solution of dyes (100 ppm, 20 ml). The system was equilibrated for 60 min at ambient temperature (25±2°) with constant stirring. The initial *p*H of the dye solutions were adjusted by adding requisite quantities of dilute hydrochloric acid or sodium hydroxide solutions. The equilibrated dye solutions were centrifuged for 20 min at 10,000 rpm in a T24 model (GDR) centrifuge. The supernatant solutions were analysed colorimetrically for residual dye concentrations at the maximum absorbance region of each dye using AIMIL MK II spectrophotometer.

Textile industrial waste water: Samples were collected from two main open drains in Jodhpur industrial area. The water was highly coloured (brownish purple), alkaline (*p*H 9.4-11.3) and foul smelling. Its detailed characteristics have been reported elsewhere[7]. The samples were allowed to stand for 4 h, the supernatant liquid decanted and *p*H adjusted to the desired level with hydrochloric acid. Different amounts of quaternary aminised $[(CH_3)_3\overset{+}{N}]$ guar derivatives were contacted with 100 ml effluent for 24 h with periodic shaking. The effluent was then centrifuged and O.D. of the supernatant liquid was measured.

Results and Discussion

The data regarding adsorption of reactive (procion orange H_2R and procion brill blue H_5G), direct (direct red and direct helio B) and hydrolysed reactive (procion red M_5B and procion brill blue MR) dyes from their aqueous solutions after treatment with different amounts of quaternary aminised guar $[(CH_3)_3\overset{+}{N}]$ derivative at *p*H 7 were plotted according to Freundlich equation;

$$X/m = KC^{\frac{1}{n}}$$

where (X/m) stands for the amount of solute (dye) per unit weight of adsorbent and C for equilibrium concentration of the dye in solution while K and n are constants. The plots of log X/m against log C in each case (Fig. 1) yielded straight lines from whose slopes and intercepts the

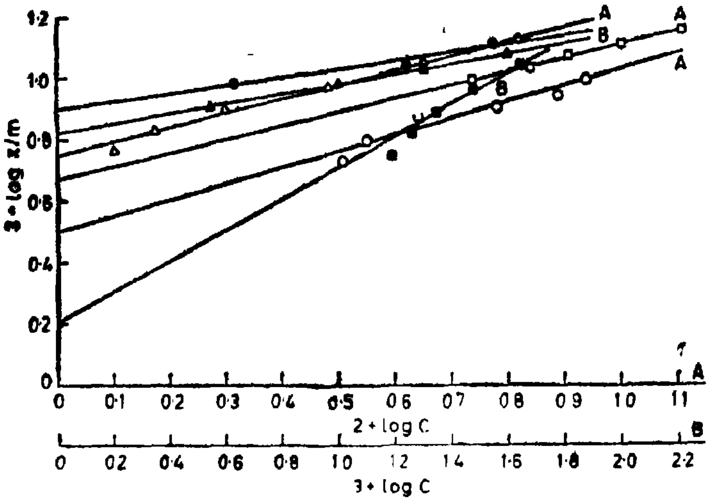


Fig. 1. log $\frac{x}{m}$ *vs* log C plot at *p*H 7 : —■—■—■— Direct helio B, —▲—▲—▲— Procion red M_8B (hydrolysed), —●—●—●— Procion orange H_2R, —□—□—□— Procion blue MR (hydrolysed), —△—△—△— Direct red, —○—○—○— Procion brill blue H_6G.

TABLE 1—ADSORPTION CAPACITY (K) AND INTENSITY OF ADSORPTION 1/n OF QUATERNARY AMINISED [$(CH_3)_3N^+$] GUAR DERIVATIVE CONTACTED WITH DIFFERENT ANIONIC DYES AT *p*H 7

Sl. no.	Dye used	Adsorption capacity K×10⁶		Intensity of adsorption 1/n	
		Graphical	Calcd.	Graphical	Calcd.
1.	Procion brill blue H_7G	3.16	3.21	0.52	0.51
2.	Procion orange H_2R	7.94	7.32	0.25	0.15
3.	Direct helio-B	1.70	1.07	0.50	0.62
4.	Direct red	5.62	5.54	0.46	0.46
5.	Procion red M_8B (hydrolysed)	6.60	6.44	0.16	0.16
6.	Procion blue MR (hydrolysed)	4.67	4.63	0.44	0.43

values of 1/n and K were obtained. The values calculated by least square method were in good agreement with the observed values (Table 1).

Influence of pH : The effect of *p*H on the adsorption was studied on the direct helio B dye using quaternary aminised guar [$(CH_3)_3\overset{+}{N}$] derivative as the adsorbent. The values of K and 1/n at *p*H 3, 5, 7 and 10 were calculated and are given in Table 2. From these values it is apparent that the adsorption of dye increases with decrease in *p*H.

TABLE 2—ADSORPTION CAPACITY (K) AND INTENSITY OF ADSORPTION 1/n OF QUATERNARY AMINISED [$(CH_3)_3N^+$] GUAR DERIVATIVE CONTACTED WITH HELIO-B AT DIFFERENT *p*H

Sl. no.	*p*H	Adsorption capacity K×10⁶		Intensity of adsorption 1/n	
		Graphical	Calcd.	Graphical	Calcd.
1.	3	3.09	2.94	0.42	0.44
2.	5	2.09	2.13	0.47	0.48
3.	7	1.70	1.08	0.50	0.62
4.	10	1.35	1.36	0.54	0.54

The mechanism of adsorption may be considered as a mixed effect of the classical and chromatographic adsorption. The improved adsorption at lower *p*H may be explained on the assumption that the adsorbent is anionic in nature due to the presence of hydroxyl groups of guar. Further, some negative sites are also introduced as galactomannons are susceptible to air oxidation in alkaline medium leading to the generation of acidic end groups[6]. These and other anionic groups are neutralised by protonation at low *p*H, which facilitates the diffusion of dye molecules in the vicinity of the adsorbent.

The reduced adsorption at higher *p*H can be due to the abundance of OH^- and consequent ionic repulsion between the surface partial negative charge on the adsorbent and anionic dye molecules. However, the introduction of positively charged substituent group [$(CH_3)_3\overset{+}{N}$] imparts strongly basic anion exchange character and enhances the adsorption capacity of the adsorbent even in alkaline medium. Hence, the synthesised quaternary aminised guar [$(CH_3)_3\overset{+}{N}$] derivative is able to adsorb the dye at higher *p*H region also.

Effect of substituents : To study the effect of substituent groups on the adsorption of dyes,

TABLE 3—ADSORPTION CAPACITIES (K) AND INTENSITY OF ADSORPTION 1/n OF DIFFERENT GUAR DERIVATIVES CONTACTED WITH DIRECT RED DYE AT pH 7

Sl. no.	Derivative	Adsorption capacity K × 10^6		Intensity of adsorption 1/n	
		Graphical	Calcd.	Graphical	Calcd.
1.	Cross-linked guar	1.20	1.20	0.50	0.52
2.	Diethylaminohydroxypropyl	1.74	1.73	0.46	0.47
3.	Quaternary aminised $[(CH_3)_3\overset{+}{N}]$	2.19	2.22	0.70	0.67
4.	Quaternary aminised $[(C_2H_5)_3\overset{+}{N}]$	3.02	3.08	0.88	0.88

the cross-linked guar was also substituted with $[(C_2H_5)_3\overset{+}{N}]$ and $[(C_2H_5)_2N]$ groups. The adsorption behaviour of these derivatives, trimethyl aminised derivative and cross-linked guar were studied with direct red dye at pH 7 under identical experimental conditions. The K and 1/n values obtained from the respective plots are given in Table 3. The value of 1/n is less than unity showing a favourable adsorption for all these derivatives at pH 7. The adsorption capacity was found[6] to be in the following order.

$[(CH_3)_3\overset{+}{N}]$-guar > $[(C_2H_5)_3\overset{+}{N}]$-guar > $[(C_2H_5)_2N]$-guar > cross linked guar.

This is in good agreement with the values of salt splitting capacities of these derivatives (0.62. 0.28, 0.13 and zero meq/g, respectively). The lower adsorption capacity of cross-linked and $[(C_2H_5)_2N]$-guar derivatives can be attributed to the absence of any positive charge.

Effect of initial dye concentration: The effect of initial dye concentration on the removal efficiency of the adsorbent $[(CH_3)_3\overset{+}{N}]$-guar derivative was studied at three different pH (3, 5 and 7) with procion brill orange H_2R and direct red dye at pH 7 only. The values of K (adsorption capacity) and 1/n were calculated from the plots of log X/m *vs* log C at 100 and 150 ppm concentrations. The results of direct red dye are given in Fig. 2. The values of K as determined by the plots, were found to be higher at initial lower concentrations of the dye concerned. This appears to be due to the abundant availability of the adsorbent surface to the dye molecules at lower concentrations.

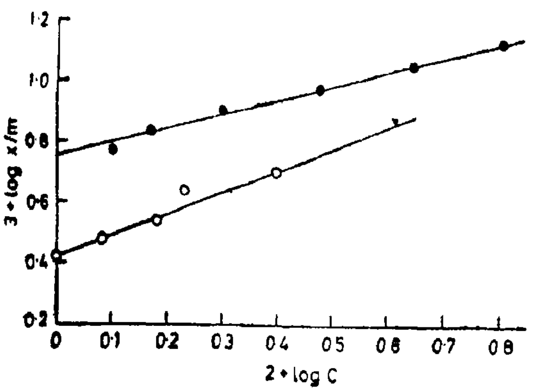


Fig. 2. Effect of initial dye (direct red) concentration on adsorption : —●—●—●— 100 ppm, —○—○—○— 150 ppm.

Studies with textile effluent: The adsorption of colour in the textile effluent by quaternary aminised $[(CH_3)_3\overset{+}{N}]$ derivative was studied at different pH. The percentage decrease in O.D., which is a measurement of total dye concentration in the effluent at different pH was plotted against the

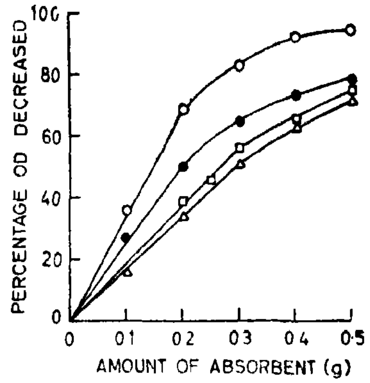


Fig. 3. Effect of pH on decrease in O.D. of textile effluent : —○—○—○— pH 3, —●—●—●— 5, —□—□—□— 7, —△—△—△— 10.

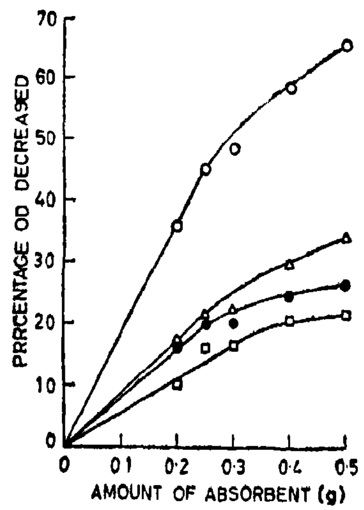


Fig. 4. Decrease in O.D. of effluent by different guargum derivatives at pH 5 : —○—○—○— Quaternary aminised $[(CH_3)_3N^+]$-guar derivative, —△—△—△— Quaternary aminised $[(C_2H_5)_3N^+]$-guar derivative, —●—●—●— Diethylaminohydroxy propyl guar derivatives, —□—□—□— Cross linked guar.

amount of derivative added (Fig. 3). The percentage decrease in O.D. appears to be maximum at lower *p*H. This is also in accordance with our observation with direct helio B dye (Table 2).

To calculate the minimum amount required to remove maximum colour from the effluent, the percentage removal of O.D. were plotted against the amount of different adsorbents at *p*H 5, which was selected as the suitable *p*H (Fig. 4). The figure shows that, at lower concentrations of colour constituents in the effluent, the percentage decrease in O.D. is proportional to the amount of adsorbent added. At higher concentrations the percentage decrease tends to reach a limiting value. Further, higher amounts of adsorbent do not decrease the O D. of the effluent proportionaly.

Conclusion : The findings of this study are

(i) Guargum derivatives are fairly good adsorbent for the removal of colour due to their capacity to remove all the classes of anionic dyes and other organic toxic constituents of textile effluent.

(ii) The percentage removal of colour is dependent on *p*H, initial dye concentrations and the substituent group on guar.

(iii) The treatment of textile effluent is simple and treated water can be reused in the textile industry.

These adsorbents being cheap, harmless and biodegradable, eliminate the problems of regeneration and disposal.

Acknowledgement

One of the authors (S.L.K.) is thankful to the U.G.C., New Delhi for awarding Teacher Fellowship and also to Director, College Education, Rajasthan for sanctioning academic leave.

References

1. G. J. Parish, *Rev. Prog. Coloration*, 1976, **55**, 7.
2. M. Dave, M. Tech. Thesis, I.I.T. Kanpur, 1979.
3. V. V. Sethuraman and B. C. Raymaheshay, *Inst. Eng. (India), Environ. Eng. Div., Part ENI*, 1980, **61**, 19.
4. V. L. Sndeyink, B. R. Kim, P. L. Hinrichs and R. A. Jennings, *Chem. Abstr.*, 1975, **82**, 34770.
5. M. Yuosa, Y. Ohba, M. Ito and K. Köhayashi, *Chem. Abstr.*, 1975, **83**, 17302.
6. R. C. Kapoor, S. L. Kalani and A. Prakash, submitted for publication.
7. R. C. Kapoor, J. Kishan, K. C. K. Mathur, P. Sharma and M. Mathur, Proceedings of the 5th Miami International Conference on Alternative Energy Sources, 1982.
8. R. A. Young and L. Liss, *Cellul. Chem. Technol.*, 1978, **12**, 399.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 604-606

Synthesis of Some New 2-[2-(5-Phenyl-3-isoxazolyl) phenoxy methyl]-4*H*-1-benzopyran-4-ones

PETER S. FERNANDES* and (Ms.) NEELAM V. GAWRI

Nadkarny-Sacasa Research Laboratory, St. Xavier's College, Bombay-400 001

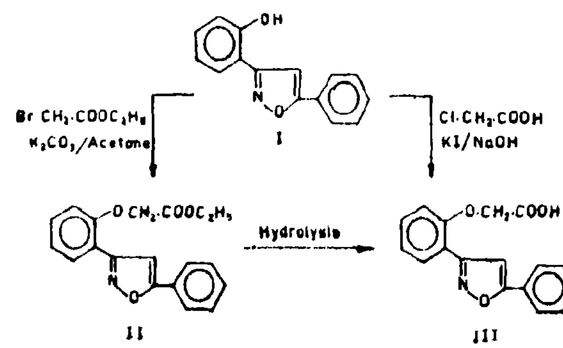
Manuscript received 16 June 1983, revised 30 January 1984, accepted 30 May 1984

The synthesis of a few new 4*H*-1-benzopyran-4-ones having substituents containing heterocyclic systems starting from [2-(5-phenyl-3-isoxazolyl)phenoxy]-acetic acid and 2-hydroxy, 2,4-dihydroxy, 2,4,6-trihydroxy acetophenones has been described.

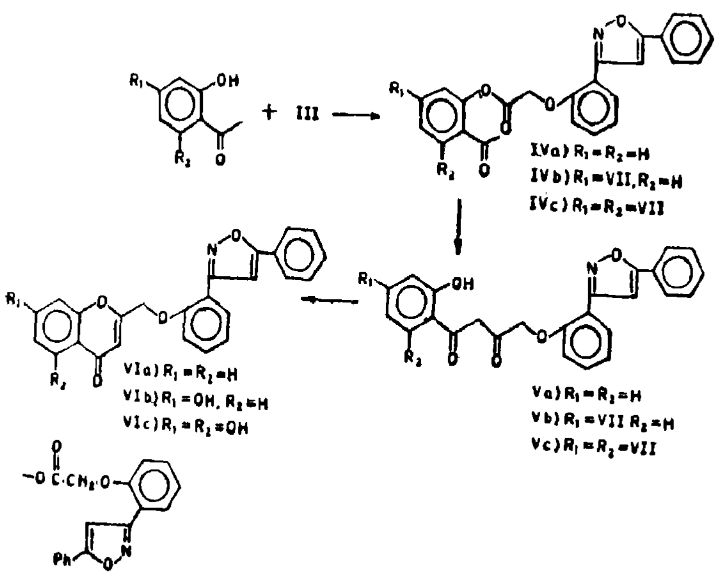
A review of chemical literature reveals that no hetero substituted derivatives at 2-position of 4*H*-1-benzopyran-4-one have been reported except a few chromones[1-7] with aliphatic substituents at 2- or 3-position of 4*H*-benzopyran-4-one.

In the previous communications we described the syntheses of chromones having substituents with pyrazole[8] and pyrazoline[9] moieties attached at 2-position of 4*H*-1-benzopyran-4-one. As a part of our continuing interest we now describe another series of chromone having [2-(5-phenyl-3-isoxazolyl) phenoxy methyl] group attached to 2-position of 4*H*-1-benzopyran-4-one.

2-(5-Phenyl-3-isoxazolyl) phenol (I), starting material for the present synthesis, was prepared by the action of hydroxylamine hydrochloride either on flavone[10] or its parent compound, β-diketone[11] in presence of pyridine. The acid[12] (III) required for the preparation of the chromones was prepared either directly by the condensation of isoxazole (I) with chloroacetic acid in presence of potassium iodide and alkali or *via* its ester (II) prepared similarly (Scheme 1). [2-(5-Phenyl-3-isoxazolyl) phenoxyl] acetic acid (III) was condensed with appropriate hydroxy acetophenone using phosphorus oxychloride[10] in pyridine to obtain phenoxy esters (IVa-IVc). These phenoxy esters were subjected



Scheme 1



Scheme 2

to Baker-Venkataraman rearrangement to yield 1,3-diketo compounds (Va-Vc), which on cyclisation yielded the 2-substituted heteroanalogues of 4*H*-1-benzopyran-4-ones or chromones (VIa-VIc) (Scheme 2).

Experimental

M.ps. were determined in open capillary tubes and are uncorrected. The structures were supported by elemental analysis, tlc and VI (a-c) by uv (MeOH) and ir (KBr, nujol) spectral data as well.

Preparation of 2-(5-phenyl-3-isoxazolyl) phenol (**I**) : A mixture of flavone (1 g) and hydroxylamine hydrochloride (1.5 g) in pyridine (10 ml) was refluxed for 6 h on a sand bath. It was then poured over ice and neutralized with cold dilute hydrochloric acid. The solid separated, was filtered and washed with water. It was purified by dissolving in sodium hydroxide solution and reprecipitating with hydrochloric acid. The solid obtained was filtered, washed with water, and crystallised from acetone to yield the product as colourless needles (62%), m.p. 235° (Found : C, 75.76 ; H, 4.71 ; N, 5.99. $C_{15}H_{11}NO_2$ requires C, 75.95 ; H, 4.64 ; N, 5.91%).

The compound was also prepared by a similar condensation using 2-hydroxydibenzoylmethane instead of flavone.

Preparation of ethyl [2-(5-phenyl-3-isoxazolyl)-phenoxy] acetate (**II**) : 2-(5-Phenyl-3-isoxazolyl) phenol (0.01 mol), and ethylbromoacetate (0.012 mol) were dissolved in dry acetone (20 ml). To this solution fused potassium carbonate (3 g) was added, and the reaction mixture was refluxed overnight on a water bath maintaining anhydrous conditions. The mixture was filtered and the residue washed with acetone. From the total extract acetone and excess of ethyl bromoacetate were removed by distilling under vacuum. The solid residue left behind was crystallised from ethanol to yield the product (82%), m.p. 95°.

Preparation of [2-(5-phenyl-3-isoxazolyl)-phenoxy] acetic acid (**III**) : [2-(5-Phenyl-3-isoxazolyl)-phenoxy] acetate (0.005 mol) was dissolved in ethanol (5 ml) and sodium hydroxide (1%, 25 ml) was added. The mixture was refluxed for 2 h. The reaction mixture was cooled and neutralized with cold dilute hydrochloric acid. The precipitate was filtered, washed with water, dried and crystallised from methanol to yield the product (56%), m.p. 178° (Found : C, 69.21 ; H, 4.35 ; N, 4.79. $C_{17}H_{13}NO_4$ requires C, 69.15 ; H, 4.41 ; N, 4.75%).

Method B : To a solution of monochloroacetic acid (0.0025 mol) in sodium hydroxide solution (0.005 mol) was added powdered potassium iodide (0.0025 mol) and refluxed for 0.5 h. To this solution **I** (0.002 mol) was added and the solution was refluxed for 1.5 h. It was filtered and the filtrate acidified with cold dilute hydrochloric acid. The solid separated was filtered, washed with water and crystallised from methanol to yield the product (50%).

The acid obtained by both the methods were identical by their m.p., and m.m.p. was undepressed in admixture with the sample prepared from method A and method B and in co- tlc.

Preparation of the esters (**IVa-IVc**) (*general procedure*) : **III** (0.007 mol) and substituted hydroxy acetophenone (0.0065 mol) were dissolved in dry pyridine (10-12 ml) and phosphorus oxychloride (0.4 ml) was added dropwise with constant stirring in cold condition. The mixture was stirred at room temperature maintaining the anhydrous condition with warming at intervals for 8 h. It was then treated with cold dilute hydrochloric acid. The solid separated was filtered, washed with cold sodium hydroxide solution followed by water. The solid obtained was crystallised from suitable solvents to yield the respective products.

2-[5-Phenyl-3-(2-phenoxyacetyloxy) isoxazole] acetophenone (**IVa**) : The solid obtained in the general procedure was crystallised from ethanol to yield the product (63%), m.p. 110° (Found ; C, 72.58 ; H, 4.63 ; N, 3.44. $C_{25}H_{19}NO_5$ requires C, 72.64 ; H, 4.60 ; N, 3.39%).

2,4-Di-[5-phenyl-3-(2-phenoxyacetyloxy)isoxazole] acetophenone (**IVb**) : The solid obtained was crystallised from ethanol giving the product (71%), m.p., 101° (Found : C, 71.48 ; H, 4.18 ; N, 3.96. $C_{42}H_{30}N_2O_9$ requires C, 71.39 ; H, 4.25 : N, 3.97%).

2,4,6-Tri-[5-phenyl-3-(2-phenoxyacetyloxy)isoxazole] acetophenone (**IVc**) : The solid obtained was crystallised from methanol to yield the product (75%), m.p. 145° (Found : C, 70.91 ; H, 4.12 ; N, 4.16. $C_{59}H_{41}N_3O_{13}$ requires C, 70.87 ; H, 4.10 ; N, 4.20%).

Preparation of 1,3-diketones (**Va-Vc**) (*general procedure*) : The esters **IVa-IVc** (0.01 mol) were dissolved in anhydrous pyridine (8 ml) and anhydrous powdered potassium hydroxide (0.001 mol) was added and the mixture stirred at room temperature. The stirring was continued (40-45 min) till the whole mass became quite viscous. The pasty mass was poured over cold water and acidified with cold dilute acetic acid (2*N*). The solid separated out was filtered, washed with water and crystallised from suitable solvents to yield the products.

Preparation of chromones (**VIa-VIc**) (*general procedure*) : 1,3-Diketo compounds (**Va-Vc**) (0.001 mol) were dissolved in glacial acetic acid (10 ml) and a few drops of concentrated hydrochloric acid was added. The reaction mixture was refluxed for 2 h. The mass was then cooled and poured over crushed ice with stirring. The solid separated was filtered and washed with cold aquous sodium bicarbonate solution (5%), followed by water. It was crystallised from suitable solvents to yield the products.

2-[2-(5-Phenyl-3-isoxazolyl) phenoxy methyl]-4H-1-benzopyran-4-one (**VIa**): The solid obtained in the general procedure was crystallised from methanol-dimethylformamide mixture to yield the product (52%), m.p. 210° (Found: C, 75.92; H, 4.32; N, 3.51. $C_{25}H_{17}NO_4$ requires C, 75.95; H, 4.30; N, 3.54%); λ_{max} 270 and 320 nm; ν_{max} 1640 (C=O), 1600 (γ-pyrone), 1260, 1140 (ether linkage) and 1660 cm^{-1} (C=N, isoxazole).

7-Hydroxy-2-[2-(5-phenyl-3-isoxazolyl] phenoxy methyl]-4H-1-benzopyran-4-one (**VIb**): The solid was crystallised from methanol-chloroform mixture to yield the product (69%), m.p. 161° (Found: C, 72.92; H, 4.11; N, 3.36. $C_{25}H_{17}NO_5$ requires C, 72.92; H, 4.14; N, 3.41%); λ_{max} 275 and 315 nm; ν_{max} 3150 (O-H), 1640, 1620 (C=O), 1600 (γ-pyrone), 1250 (ether linkage) and 1660 cm^{-1} (C=N, isoxazole).

5,7-Dihydroxy-2-[2-(5-phenyl-3-isoxazolyl) phenoxy methyl]-4H-1-benzopyran-4-one (**VIc**): The solid was crystallised from methanol to yield the product (65%), m.p. 181°(Found: C, 70.32; H, 3.95; N, 3.21. $C_{25}H_{17}NO_6$ requires C, 70.26; H, 3.98; N, 3.28%); λ_{max} 275 and 315 nm; ν_{max} 3200 (O-H), 1590 (C=O), 1605 (γ-pyrone), 1220, 1150 (ether linkage) and 1640 cm^{-1} (C=N, isoxazole).

All the above compounds (VIa-VIc) gave single spot on tlc and showed bluish yellow fluorescence under uv light.

Acknowledgement

One of the authors (P.S.F.) thanks the U.G.C., New Delhi for financial assistance.

References

1. E. EIDEN and D. DOLCHER, *Arch. Pharm. (Weinheim, Ger.)*, 1975, **308**, 385.
2. J. SCHMUTZ, R. HIRT, F. KUNZLE, E. EICHENBERGER and H. LAUENER, *Helv. Chim. Acta*, 1953, **36**, 620.
3. A. WANDER, Brit. Pat. 728767 / 1956 (*Chem. Abstr.*, 1956, **50**, 7876).
4. J. SCHMUTZ, R. HIST and H. LAUNER, *Helv. Chem. Acta*, 1952, *35*, *1168*.
5. R. C. JOHNSTON and D. KIDD, *J. Chem. Soc.*, 1964, 4730.
6. A. I. TOLMACHER, V.P. SRIBNAYA and L. V. SHEHEGLOVA, *J. Gen. Chem. USSR (Engl. Transl.)*, 1963, **33**, 433.
7. A. I. KIPRIANOV and A. I. TOLMACHER, *J. Gen. Chem. USSR (Engl. Transl.)*, 1960, **30**, 659.
8. P. S. FERNANDES, D. DESAI and V. V. NADKARNY, *J. Indian Chem. Soc.*, 1983, **50**, 165.
9. P. S. FERNANDES and E. D. L. M. MENDES, *J. Indian Chem. Soc.*, 1983, **60**, 967.
10. P. N WADODKAR and M. G. MARATHY, *Indian J. Chem.*, 1972, **10**, 45.
11. W. BAKER, J. HARBORNE and W. OLLIS, *J. Chem. Soc.*, 1952, 1303.
12. N. GAWRI, M.Sc. Thesis, University of Bombay, 1983.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 607-608

4-Thiazolidinones as Potential Antibacterial and Antitubercular Agents

N. C. DESAI, H. K. SHUKLA, R. R. ASTIK and K. A. THAKER

University Department of Chemistry, Bhavnagar University, Bhavnagar-364 002

Manuscript received 6 August 1982, revised 30 March 1984, accepted 17 June 1984

2-Aryl-3-[3-(4-methyl/methoxyphenyl)-thiazolidine-2,4-dione-5-yl]-4-thiazolidinones have been prepared from the reaction of thioglycolic acid with azomethines in dry benzene. The azomethines have been prepared by condensation of different aromatic aldehyde with 5-amino-3-(4-methyl/methoxyphenyl)-thiazolidine-2,4-dione. 4-Thiazolidinones *show antibacterial activity when tested against S. aureus* and *E. coli* by nutrient agar pour plate method, and have been tested against $H_{37}R_v$ strain of *Mycobacterium tuberculosis*.

THIAZOLIDINONES belong to an important group of heterocyclic compounds, having carbonyl group at position 2, 4 or 5 is the subject of extensive study. Several substituted thiazolidinones, biologically active compounds were prepared[1,2] and found to have anaesthetic, anticonvulsant and sedative properties. Besides, these compounds having =N-C-S- grouping have antitubercular, hematocidal, anticonvulsant, herbicidal, antifungal, insecticidal, hypnotic, anthelmintic, cardiovascular and antibacterial properties[3-13]. We have prepared 2-aryl-3-[3-(4-methyl/methoxyphenyl)-thiazolidine-2,4-dione-5-yl]-4-thiazolidinones. 5-Amino-3-(4-methyl/methoxyphenyl)-thiazolidine-2,4-dione have been prepared by the reported method[14]. Elemental analysis was carried out on semi-micro C, H, N analyser. The ir spectra (KBr) were taken on Perkin-Elemer 137 G spectrometer.

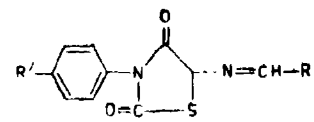
Experimental

Preparation of Schiff bases: 5-Amino-3-(4-methyl/methoxyphenyl)-thiazolidine-2,4-dione (0.01 mol) was dissolved in ethanol (50 ml, 95%) and aromatic aldehyde (0.01 mol) added and refluxed on water-bath for 3 h. The product was distilled until Schiff base commenced to crystallise (Table 1).

Preparation of 4-thiazolidinones: To the Schiff base (0.01 mol) in benzene (25 ml) was added thioglycolic acid and the contents refluxed for 8 h until water collected in Dean and Stark trap. Excess of benzene was removed, treated with saturated solution of $NaHCO_3$ and extracted with ether. The ether extract was treated with dried Na_2SO_4, ether distilled off. The residue on crystallisation gave thiazolidinone (Table 2).

Pharmacological screening: 4-Thiazolidinones were screened for antituberculostatic and antibacterial activity against *E. coli* and *S. aureus* (Table 2).

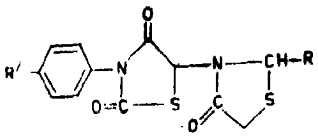
TABLE 1—SCHIFF BASE COMPOUNDS



Sl. no.	R	R'	M.p. °C	Analysis %, Found/(Calcd.) N
1.	$-C_6H_5$	$-CH_3$	158	8.92 (9.03)
2.	$-2-OH.C_6H_4$	,,	132	8.21 (8.58)
3.	$-5-Br-2-OH.C_6H_3$	,,	172	7.11 (6.91)
4.	$-3,5-diBr-2-OH.C_6H_2$	,,	135	6.01 (5.78)
5.	$-4-OCH_3.C_6H_4$	,,	121	9.02 (8.64)
6.	$-2-Cl.C_6H_4$	,,	138	7.91 (8.12)
7.	$-4-NO_2.C_6H_4$	,,	191	11.93 (11.79)
8.	$-3-NO_2.C_6H_4$	,,	164	11.96 (11.79)
9.	$-3-OCH_3-4-OH.C_6H_3$	,,	172	7.52 (7.86)
10.	$-C_6H_5$	$-OCH_3$	131	8.69 (8.58)
11.	$-2-OH-C_6H_4$	,,	122	8.14 (7.82)
12.	$-4-OCH_3.C_6H_4$	,,	139	7.52 (7.86)
13.	$-4-Cl.C_6H_4$	,,	152	8.02 (7.79)
14.	$-3-NO_2.C_6H_4$	,,	128	10.55 (10.82)
15.	$-3,5-diBr-2-OH-C_6H_2$	,,	170	5.52 (5.38)

In vitro antitubercular activity of the hitherto synthesised hydrazones and 4-thiazolidinones was studied against $H_{37}R_v$ strain of *Mycobacterium tuberculosis* in Lowenstein-Jensen egg media at 0.02 $\mu g\ ml^{-1}$. The retardation of the growth rate has been studied upto six weeks at 37°.

TABLE 2 — 4-THIAZOLIDINONES



Sl. no.	R	R′	ν_{max} cm^{-1}	M. p. °C	Anilysis % ; Found/(Calcd.) N	Antibacterial activity *S. aureus*	Antibacterial activity *E. coli*	*M. tuberculosis** $H_{37}R_v$
1.	$-C_6H_5$	$-CH_3$		140	7.56 (7.29)	–	–	+
2.	$-2-OH.C_6H_4$	,,	3588 (OH) 1730 (C=O) 1220 (4 TR)	170	6.89 (7.00)	+	–	+
3.	$-5-Br-2-OH.C_6H_3$	,,		132	6.01 (5.34)	+	–	+
4.	$-3,5-diBr-2-OH.C_6H_2$	,,		122	5.21 (5.01)	++	+	+
5.	$-4-CH_3.C_6H_4$	,,		159	7.32 (7.03)	+	+	+
6.	$-2-Cl.C_6H_4$	,,		183	6.84 (6.69)	–	–	+
7.	$-4-NO_2.C_6H_4$	,,		170	9.58 (9.97)	+	–	+
8.	$-3-NO_2.C_6H_4$	,,		180	9.52 (9.97)	+	–	+
9.	$-3-OCH_3-4-OH.C_6H_3$	,,	3595 (OH) 1742 (C=O) 1200 (4 TR)	192	6.82 (6.51)	+	+	+
10.	$-C_6H_5$	$-OCH_3$	850 ($-C_6H_5$) 1750 (C=O) 1310 (4 TR)	154	7.32 (7.00)	–	–	+
11.	$-2-OH.C_6H_4$	,,	3570 (OH) 1720 (C=O) 1325 (4 TR)	134	6.53 (6.73)	+	–	+
12.	$-4-OCH_3.C_6H_4$	,,		118	6.78 (6.51)	+	–	+
13.	$-4-Cl.C_6H_4$	,,		200	6.68 (6.44)	+	+	+
14.	$-3-NO_2.C_6H_4$	,,		142	9.12 (9.43)	–	–	+
15.	$-3,5-diBr-2-OH.C_6H_2$	,,		190	5.03 (4.71)	++	+	+

All compounds gave satisfactory C, H, S analyses.
4 TR = 4-Thiazolidinone ring system.
(+) = Zone dia. less than 20 mm.
(++) = Zone dia. more than 20 mm.
*Concentration 0.02 $\mu g\ ml^{-1}$.

The antibacterial activity was tested by nutrient agar pour plate method in dimethyl formamide and found to be active against *E. coli* and *S. aureus* organisms in various concentrations.

Acknowledgement

The authors are thankful to Bhavnagar University for Junior Research Fellowship to two of them (N.C.D. and H.K.S.) and also to Dr. S. B. Trivedi, Director, Tuberculosis Research Centre, Amargadh, for screening the sample.

References

1. A. R. SURREY, *J. Am. Chem. Soc.*, 1949, **71**, 3354.
2. H. D. TRAUTMAN and L. M. LONG, *J. Am. Chem. Soc.*, 1948, **70**, 3436.
3. H. K. SHUKLA, R. R. ASTIK and K. A. THAKER, *J. Indian Chem. Soc.*, 1981, **58**, 1182.
4. A. J. COWPER, R. R. ASTIK and K. A. THAKER, *J. Inst. Chem., Calcutta*, 1981, **53**, 111.
5. S. NAGAR, H. H. SINGH, J. N. SINHA and S. S. PARMAR, *J. Med. Chem.*, 1973, **16**, 178.
6. H. C. TONG and D. SKIDMOVE, *Mosc. News*, 1975, **35**, 76 (*Chem. Abstr.*, 1975, **83**, 109744).
7. G. R. HENDRICKS, *J. Med. Pharm. Chem.*, 1965, **8**, 762.
8. H. D. TRAUTMAN and L. M. LONG, *J. Am. Chem. Soc.*, 1951, **66**, 329.
9. F. C. BROWN, *Chem. Rev.*, 1961, **61**, 463.
10. K. A. ZOLOTOREVA, I. P. MASLOVA, N. A. GLAZUNOVA, E. F. BURMISTROV and L. A. PUGACHEVA, *Voronezh.*, 1964, **5** (*Chem. Abstr.*, 1966, **65**, 18767).
11. G. DANILA, *Rev. Chim. (Bucharest)*, 1978, **29**, 820 (*Chem. Abstr.*, 1979, **90**, 72086).
12. G. DANILA, *Rev. Chim. (Bucharest)*, 1978, **29**, 1152 (*Chem. Abstr.*, 1979, **90**, 152037).
13. S. P. SINGH, S. S. PARMAR, KRISHAN RAMAN and V. L. STENBERG, *Chem. Rev.*, 1981, **81**, 175.
14. P. R. SINGH, *Indian J. Chem.*, 1963, **1**, 100.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 609-610

Preparation and Antitubercular Activity of Some 1-(4-Amino-3,5-dibromo)-2-benzalhydrazine and 1-[4-(Phenylthioureido-3,5-dibromobenzoyl)]-2-substituted-benzalhydrazines

M. P. DAVE, J. M. PATEL, N. A. LANGALIA and K. A. THAKER

University Department of Chemistry, Bhavnagar University, Bhavnagar-364 002

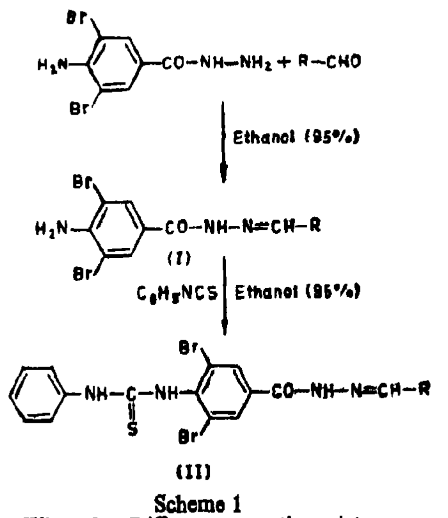
Manuscript received 12 March 1984, accepted 30 May 1984

Several 1-(4-amino-3,5-dibromo)-2-benzalhydrazine and 1-[4-(phenylthioureido-3,5-dibromobenzoyl)]-2-substituted-benzalhydrazines have been prepared and screened for their antitubercular activity against $H_{37}R_v$ strain.

THIOUREA derivatives are known to possess antitubercular[1], antibacterial and other biological activities[2-7]. Taxonomic similarity between *Mycobacteria* and fungi prompted to test the effect of some known antifungal agents against *M. tuberculosis in vitro*[8]. Among the compounds tested only certain thioureas showed tuberculostatic activity *in vitro*.

Hydrazones have been found to possess antibacterial[9], antifungal[10] and insecticidal[11] activities. Schiff bases are known to exhibit anticancer and antitubercular activities[12-13].

The present communication deals with the preparation and pharmacological studies of some 1-(4-amino-3,5-dibromo)-2-benzalhydrazine (I) and 1-[4-(phenylthioureido-3,5-dibromobenzoyl)]-2-substituted-benzalhydrazines (II). The title compounds (II) have been prepared from various 1-(4-amino-3,5-dibromo)-2-benzalhydrazines by condensation of phenylisothiocyanate and tested against $H_{37}R_v$ strain of *Mycobacterium tuberculosis*.



(II)

Scheme 1
Where R = Different aromatic moiety.

The synthetic sequence of the title compounds is presented in Scheme 1.

Experimental

Melting points of the compoundss ynthesised were determined in open capillary tubes and are uncorrected. The structure of the compounds have been established on the basis of their elemental analysis and ir spectra (KBr) using Spectromom 2000 spectrophotometer. The ir spectra of the thiourea of the title compounds show band at 1380 cm^{-1} due to -NH-CS-NH- linkage and at 3200 cm^{-1} suggesting the presence of stretching frequency of -OH of 4-hydroxybenzaldehyde.

4-Amino-3,5-dibromobenzoic acid hydrazide : 4-Amino-3,5-dibromo benzoic acid hydrazide was prepared by the reported method[14].

1 - (4-Amino-3,5-dibromobenzoyl)-2-benzalhydrazine (II) : To the solution of 4-amino-3,5-dibromo benzoic acid hydrazide (0.01 mol) in ethanol (95%, 28 ml) was added benzaldehyde (0.01 mol) in ethanol (95%, 15 ml) and the content kept for 24 h at room temperature. The solid obtained was filtered, dried and crystallised from ethanol (95%) to yield the product (62%), m.p. 245° (Found : N, 10.79%. $C_{14}H_{12}Br_2N_3O$ requires N, 10.58%).

1 - [4 - (Phenylthioureido) - 3,5 - dibromobenzoyl]-2-benzalhydrazine (II) : To the solution of 1-(4-amino - 3, 5 - dibromobenzoyl) - 2 - benzalhydrazine (0.01 mol) in ethanol (95%, 30 ml) was added phenyl isothiocyanate (0.01 mol) in ethanol (95%, 20 ml) and the contents refluxed for 45 min, cooled and filtered. The solid so obtained was washed with ether and crystallised from ethanol (95%) to yield the product (82%), m.p. 230° (Found : N, 10.75 ; S, 6.23%. $C_{21}H_{16}Br_2N_4OS$ requires N, 10.53 ; S, 6.02%).

Antimycobacterial screening : The *in vitro* antitubercular activity of the compounds I and II have been studied at 0, 5 and 30 $\mu g\ ml^{-1}$ concentration

TABLE 1—DATA OF 1-(4-AMINO-3,5-DIBROMOBENZOYL-2-BENZALHYDRAZINE (I)

Sl. no.	R	M. p. °C	Yield %	Antitubercular activity µg ml^{-1} 0	5	30
1.	Phenyl	245	62	–	–	–
2.	2-Chlorophenyl	285	70	–	–	–
3.	3-Chlorophenyl	220	64	–	–	+
4.	3-Nitrophenyl	260	68	–	–	–
5.	4-Nitrophenyl	320	59	–	–	+
6.	4-Methoxyphenyl	240	65	–	–	+
7.	2-Hydroxyphenyl	280	67	–	–	+
8.	3,5-Dibromo-2-hydroxy phenyl	281	63	–	+	+
9.	3,4-Methylenedioxy phenyl	270	72	–	+	+
10.	4-Hydroxy-3-methoxy phenyl	244	73	–	–	–
11.	4-Hydroxyphenyl	280	66	–	–	–
12.	3,4-Dimethoxyphenyl	248	71	–	–	–

All compounds gave satisfactory C, N, S analyses.
\+ Active.
– Not active.

TABLE 2—DATA OF 1-[4-(PHENYL THIOUREIDO-3,5-DIBROMO BENZOYL)]-2-SUBSTITUTED-BENZALHYDRAZINE (II)

Sl. no.	R	M. p. °C	Yield %	Antitubercular activity, µg ml^{-1} 0	5	30
1.	Phenyl	230	82	–	–	–
2.	2-Chlorophenyl	225	81	–	–	+
3.	3-Chlorophenyl	203	78	–	–	+
4.	3-Nitrophenyl	223	86	–	–	–
5.	4-Nitrophenyl	146	72	–	–	–
6.	4-Hydroxyphenyl	246	80	–	–	+
7.	4-Methoxyphenyl	179	75	–	–	+
8.	2-Hydroxyphenyl	250	83	–	–	+
9.	3,4-Methylenedioxy phenyl	144	88	–	–	+
10.	3,4-Dimethoxyphenyl	196	72	–	–	+
11.	3,5-Dibromo-2-hydroxy phenyl	138	76	–	–	+
12.	4-Hydroxy-3-methoxy phenyl	180	84	–	–	+

Notes same as in Table 1.

using dimethylformamide as solvent against $H_{37}R_v$ strain of *Mycobacterium tuberculosis* utilising Lowenstein-Jensen egg medium (4 ml). The procedure was duplicated.

The results are recorded in Tables 1 and 2.

Acknowledgement

The authors are thankful to Bhavnagar University for research facilities and research scholarships to two of the authors (M.P.D. and J.M.P.), and grateful to Dr. S. B. Trivedi, Director, Tuberculosis Research Centre, Amargadh, for providing facilities of antitubercular screening.

References

1. M. SHIMOTANI, *J. Pharm. Soc. Jpn.*, 1952, **72**, 440.
2. R. H. WILLIAMS and E. G. FRAME, *Bull. John Hopkins Hosp.*, 1945, **77**, 314.
3. D. E. BEER, E. J. BUCK, J. S. IDE and A. M. HJORT, *J. Pharmacol. Exp. Ther.*, 1936, **57**, 19.
4. O. DRESSEL, A. OSSENBECK and E. TIETZE, U.S. Pat., 1898431, 1933, (*Chem. Abstr.*, 1933, **27**, 2762).
5. S. S. GUHA SIRCAR and K. K. PATNAIK, *J. Indian Chem. Soc.*, 1950, **27**, 535.
6. N. S. DROZDOV and U. A. SKYLVAROV, *Compt. Rend. Acad. Sci., U.S.S.R.*, 1940, **6**, 694.
7. V. S. MISHRA and S. PRAKASH, *J. Indian Chem. Soc.*, 1974, **51**, 969.
8. R. L. MAYER, *Rev. Med. Franc.*, 1941, **9**, 393.
9. P. MONTEGAZZA, F. PACCHIANE and G. CAVALIND, *Antibio. Chemotherapy*, 1961, **11**, 405.
10. A. N. COST, A. A. SHUMAKOVA, E. I. KOZOLOVA and L. I. GANDBERG, *Chem. Abstr.*, 1960, **54**, 14553.
11. G. T. BOTTGER, A. P. YERINGTON and S. I. GERTLER, "Entomol and Plant Cuarantine", U.S. Dept. Agric., 1951, E. 815-17.
12. J. SEN GUPTA, *Indian J. Appl. Chem.*, 1966, **29**, 33.
13. L. MUSLIN, W. ROTH and H. ERLENMEYER, *Helv. Chim. Acta*, 1953, **36**, 886.
14. M. CLAISEN, P. VANDIJCK and H. VANDERHAEGHE, *J. Pharm. Pharmacol.*, 1954, **6**, 127.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 611-613

Synthesis of Some Substituted Anthraquinone and Acridine Derivatives and Their Antiamebic Activities

B. R. SARKAR and B. PATHAK

Department of Chemical Technology, University of Calcutta, 92, Acharya P. C. Road, Calcutta-700 009

and

B. P. DEY, S. DUTTA and S. C. LAHIRI

Department of Chemistry, Kalyani University, Kalyani-741 235

In our attempt to synthesize new compounds with antiamebic activities, some substituted anthraquinone and acridine derivatives have been made. The compounds have been subjected to *in vitro* screening using axenic cultures of *E. histolytica*. The compounds have been found to be more effective than 5-chloro-7-iodo-8-quinolinol but less effective than metronidazole.

AMEBIASIS is one of the most prevalent diseases in tropical countries. A number of useful drugs like emetine hydrochloride, iodo-chlorohydroxyquinoline and metronidazole are known but they are usually associated with adverse side effects[1-3]. Metronidalzole is at present the primary drug in the treatment of amebiasis[3,4]. But its toxic effects like cardiotoxicity[5] and malignancy[6,7] in the rodents have been reported. Thus, the search for new antiamebic drugs is urgently felt.

Many 1-substituted 4- or 5-imidazole derivatives have activity against *T. vaginalis*, *T. foetus*[8] as well as against *E. histolytica*. A monoformamidine of 2-aminoanthraquinone, reported to have antiparasitic activity[9], was inactive as amebicide. However, a series of bisamidines of 2,6-diaminoanthraquinone were found to be effective against cecal and hepatic forms of *E. histolytica* infections in rats and hamsters, respectively[10]. 2,6-Bis (1-piperidinoalkylideneamino)anthraquinone exhibited amebicidal activity[11]. It was, therefore, considered worthwhile to study the antiamebic activities of substituted anthraquinone compounds (Table 1) where the basic group is kept one c-atom away from the anthraquinone moiety. Some of the compounds may be considered to be modified imidazole derivatives. Insecticidal, bactericidal, antimalarial and local anaesthetic properties are exhibited by acridine derivatives[12-16]. The flat aromatic acridine molecule was thought to be inserted (*i.e.* intercalated) between adjacent base pairs in the double helix of DNA and the intercalating compounds inhibit DNA synthesis and DNA dependent RNA synthesis in microbial cells[17]. Synthesis of some 9-substituted acridine derivatives (Table 1) was, therefore, considered worthwhile to study their amebicidal properties.

The synthesis and *in vitro* antiamebic activities of some substituted anthraquinone and 9-substituted acridine derivatives using axenic cultures of *E. histolytica* have been reported in this communication.

Experimental

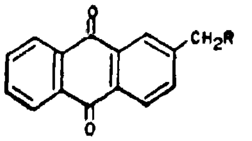
Biological activity: The *in vitro* testing of the compounds was done using axenic medium. In bacteria-associated culture of *E. histolytica*, the amebicidal activity of a test compound is influenced by various factors such as media, *p*H, oxidation-reduction potential and the bacterial flora. The variations of amebicidal end point are likely to occur in different non-axenic cultures. True chemotherapeutic activities of amebicidal agents could be made using the axenic culture of *E. histolytica*. The composition of the axenic medium was similar to that of TP-S-1 monophasic medium[18].

We, however, eliminated horse serum (or bovine serum as used[19]) as well as ascorbic acid. The bacterial flora was eradicated by treatment with gentian violet and acriflavine[20]. Sufficient NaOH (1*N*) was added to the broth to adjust the *p*H 7 or a little above. The broth was autoclaved and stored at 4°. However, the use of antibiotics was avoided.

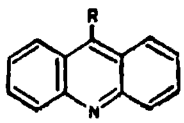
E. histolytica (L. D. strain) was grown axenically in modified TP-S-1 Diamond medium. The screw cap corning tubes (12 ml) containing 8.8 ml of the medium were incubated at 37° for 24 h to check the sterility of the medium. For ameba culture and drug testing, the reported[21,22] method was followed.

Ten days old cultures initiated from small inocula was used as seeds for inoculum. These were chilled in ice-cold water for 5 min, gently stirred and centrifuged at slow speed. The supernatant fluid was decanted off, leaving the residue in the medium in which the ameba were homogenised and counted several times with haemocytometer and the average taken.

TABLE 1—CHARACTERIZATION DATA ON 2-SUBSTITUTED ANTHRAQUINONE AND 9-SUBSTITUTED ACRIDINE



(IA Series)



(IB Series)

Sl. no.	Compound	Method of prepn.	M.p. °C	Yield %	Analysis %; Found /(Calcd.) C	H	N	Uv spectra (EtOH) λ_{max} (Log ε) nm	Minimum inhibitory concn. $\mu g\ ml^{-1}$
	IA Series R								
1.	$N(CH_3)_2$	A	90–92	40	76.60 (76.98)	5.35 (5.66)	5.12 (5.28)	256 (4.57) 326–27 (3.57)	31.3
2.	$N(C_2H_5)_2$	A	75–78	45	77.40 (77.80)	6.24 (6.48)	4.52 (4.77)	256 (4.59) 326–27 (3.60)	15.6
3.	piperidyl	A	103–105	40	78.48 (78.68)	6.05 (6.23)	4.45 (4.59)	256 (4.63) 326–328 (3.66)	62.5
4.	morpholinyl	A	100–101	30	74.04 (74.27)	5.32 (5.54)	4.26 (4.56)	256 (4.59) 326–328 (3.69)	15.6
5.	imidazolyl	B	188–190	38	74.88 (75.01)	3.85 (4.17)	9.64 (9.72)	256 (4.49) 324–326 (3.66)	31.3
6.	5-nitroimidazolyl	B	249–251	35	63.64 (63.88)	3.10 (3.30)	12.42 (12.61)	254 (4.55) 318–322 (3.78)	15.6
7.	2-methylimidazolyl	B	165–166	40	75.25 (75 50)	4.52 (4.63)	8.95 (9.27)	254 (4.49) 305–310 (3.86)	15.6
8.	2-methyl- 5-nitroimidazolyl	B	238–240	25	65.65 (65.70)	3.62 (3.75)	11.95 (12.11)	254 (4.50) 305–310 (3.87)	62.5
	IB Series								
9.	–imidazolyl	C	334–335	20	77.94 (78.36)	4.35 (4.49)	16.90 (17.14)	253 (4.80) 379 (2.92) 397 (3.90)	62.5
10.	5-nitroimidazolyl	C	337° (volatile)	20	65.98 (66.21)	3.23 (3.45)	19.12 (19.32)	253 (4.89) 380 (3.17) 398 (3.98)	15.6
11.	2-methylimidazolyl	C	219–221	25	78.65 (78.75)	4.98 (5.02)	15.96 (16.21)	251 (5.02) 359 (3.95) 383 (3.66)	31.3
12.	2-methyl- 5-nitroimidazolyl	C	241–243	22	67.05 (67.10)	3.85 (3.95)	18.21 (18.42)	251 (4.08) 300–302 (3.95)	31.3
13.	5-chloro-7-iodo- 8-quinolinol	—	—	—	—	—	—	—	62.5
14.	Metronidazole	—	—	—	—	—	—	—	3.9

Seven days' old culture was used as inoculum and the tubes containing $\sim 20\times10^4$ amebae ml^{-1} were used for drug testing. 0.2 ml amebic suspension was used for inoculation. 1ml drug suspension in normal saline was added to 9 ml (containing 8 8 ml of medium +0.2 of inoculum) in each culture tube in duplicate to give a drug concentration 1000 $\mu g\ ml^{-1}$ Eight successive two fold serial dilutions of the drug in normal saline were made and the drugs were added in the way described before in subsequent duplicate tubes. Strict aseptic condition was maintained. Drug dilutions were sterilized by autoclaving at 10 lbs/sq. inch for 15 min before test. The tests were run for 48 h and incubation carried out at 37°.

The cultures were examined after 48 h for viable and motile amebae and amebicidal end points were noted. The results were further confirmed by subculture. The operations were repeated for confirming the reproducibility of results.

Preparation and characterization of compounds: The uv spectra of the compounds were recorded with Perkin-Elmer-Hitachi 200 spectrophotometer. Melting points were determined using Gallenkamp melting point apparatus and are uncorrected.

2-Bromomethylanthraquinone (m.p. 200-205°) was prepared from 2-methylanthraquinone by the action of *N*-bromosuccinimide and traces of benzoyl peroxide in dry CCl_4[8]. The 2-bromomethylanthraquinone was then allowed to react with the appropriate amine by the following methods.

Method A: Equimolar bromo-compound and the amine were refluxed on water bath for 4 h in sealed tubes and the content were then poured in water. The solid compound separated was dissolved in dilute HCl, extracted with ether and the acidic solution was basified with liquor NH_3. The compound separated was washed with water, dried and crystallized from dilute alcohol.

Method B: Equimolar halo-compound and the imidazole derivative were dissolved in minimum volume of DMF and the solution was kept on boiling water bath for 3 h and then in oil bath so that DMF boiled gently. Finally it was acidified with dilute HCl and extracted with ether. Aqueous acidic solution was basified with liquor NH_3 when a solid separated. The solid was filtered out, washed with water, dried and the product was crystallized from dilute alcohol.

Method C: A mixture of 9-chloroacridine and imidazole derivative (0.005 mol each) was refluxed with phenol (5 ml) in an oil bath for 24 h. The mass was then acidified with dilute HCl, phenol was extracted out with ether, the aqueous acid layer was basified with liquor NH_3 and the material was filtered out. The product was crystallized from alcohol.

The characterization data of the compounds, their absorption maxima and antiamebic end points are recorded in the Table 1. *In vitro* antiamebic end points of some typical drugs in axenic medium were also recorded for comparison. The absorption maxima contains the characteristic bands of athraquinone and acridine molecules which shifted towards the long wavelength region.

Discussion

The reasons for the antiamebic activities of the compounds are not known. But the reasons may be due to penetration of these water insoluble compounds into the protozoal cells. It is also known that the compounds which have shown to bind the DNA by intercalation have generally been condensed tricyclic aromatics with atleast one basic function[24,25]. Thus, the activities of the compounds may be due to binding of DNA by intercalation though we could not adduce sufficient evidence in favour of this hypothesis.

Acknowledgement

One of the authors (B.R.S.) thanks the U.G.C., New Delhi for financial assistance.

References

1. J. P. Canby and F. H. Ariz, *J. Am. Med. Assoc.*, 1974, 230, 538.
2. L. S. Fischer, A. W. Chow, L. Lindquist and L. B. Guce, *Am. J. Med. Sci.*, 1976, 271, 65.
3. G. P. Dutta, "Experimental and Clinical Studies on Ameobiasis", Tata McGraw-Hill, 1981.
4. WHO Tech. Rep., Ser. 421, 1969, 5-52; "Pharmacological Basis of Therapeutics", ed. L. Goodman and A. Gillman, 5th. ed., MacMillan, New York, 1975, Chapter 54.
5. S. J. Powell, *Am. J. Trop. Med. Hyg.*, 1967, 16, 447.
6. M. Rustin and P. Shubik, *J. Natl. Cancer Inst.*, 1972, 48, 721.
7. H. B. Stone and H. R. Withers, *J. Natl. Cancer Inst.*, 1975, 55, 1189.
8. H. N. Prince, E. Grunberg, E. Titsworth and W. F. Lorfnzo, *Appl. Microbiol.*, 1969, 18, 728.
9. N. Steiger and N. J. Nutley, U. S. Pat., 3184482/1965.
10. P. F. Fabio, T. L. Fields, Yang-I-Lin, E. J. Burden, S. Carvajal, K. C. Murdock and S. A. Lang, Jr., *J. Med. Chem.*, 1978, 21, 273.
11. S. A. Lang, Jr., P. F. Fabio, Yang-I Linn, K. C. Murdock and T. L. Fields, U. S. Pat. 4118498, 1978 (*Chem. Abstr.*, 1979, 90, 54836); U. S. Pat. 4131676, 1978 (*Chem. Abstr.*, 1979, 90, 151886); U. S. Pat. 4141992, 1979 (*Chem. Abstr.*, 1979, 90, 168374).
12. J. H. Burkhalter, F. H. Tendick, E. M. Jones, P. A. Jones, W. F. Holcomb and A. L. Rawlins, *J. Am. Chem. Soc.*, 1948, 70, 1363.
13. V. K. Mehta and S. R. Patel, *J. Indian Chem. Soc.*, 1966, 43, 235.
14. A. S. Samarin, N. A. Samarina, Yu. A. Kozhevnikov and E. L. Pidemskil, *Sb. Nauk. Tr. Ferm. Politekh. Inst.*, 1965, 18, 155 (*Chem. Abstr.*, 1967, 66, 28637).
15. A. S. Samarin and T. A. Vereiskaya, *Sb. Nauk. Tr. Ferm. Politekh. Inst.*, 1965, 18, 148 (*Chem. Abstr.*, 1967, 66, 46312).
16. V. I. Bliznyukov and V. P. Shtuchna, *Farm. Zhur.* (*Kiev*), 1961, 16, 12.
17. A. R. Peacocke and J. N. H. Skerett, *Trans. Farad. Soc.*, 1956, 32, 261.
18. L. S. Diamond, *J. Parasitol*, 1968, 54, 715.
19. G. P. Dutta and V. K. Mohan Rao, *Indian J. Microbiol.*, 1966, 6, 83.
20. S. R. Das and B. N. Singh, *Proc. Natl. Acad. Sci. India, Sect. B*, 1970, 36, 159.
21. J. N. S. Yadava and G. P. Dutta, *Indian J. Med. Res.*, 1973, 61, 971.
22. B. R. Sarkar, B. C. Pathak, S. Dutta and S. C. Lahiri, *J. Indian Chem. Soc.*, 1984, 61, 151.
23. M. D. Bhaskar, B. D. Tilak and K. Venkataraman, *J. Sci. Ind. Res.* (*B*), 1957, 16, 392.
24. S. Neidle, *Prog. Med. Chem.*, 1979, 16, 151.
25. H. S. Schwartz, *Adv. Cancer*, Chemother, 1970, 1, 1.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 614-616

Extraction, Spectrophotometric and Fluorimetric Determination of Submicrogram Quantities of Aluminium with *N*-Phenylbenzohydroxamic Acid and Morin

Y. K. AGRAWAL and A. K. NAGAR

Analytical Laboratories, Pharmacy Department, Faculty of Technology & Engineering, M. S. University of Baroda, Kalabhavan, Baroda-390 001

Manuscript received 5 September 1983, accepted 26 May 1984

The spectrophotometric and fluorimetric method for the determination of aluminium(III) with *N*-phenylbenzohydroxamic acid (PBHA) and morin have been developed. The determination is based on the extraction of aluminium-PBHA complex into chloroform in ammonium carbonate medium and then forming its complex with morin. The greenish yellow coloured aluminium-PBHA-morin complex has a maximum absorbance at 430 nm with a molar absorptivity 1.2×10^4 l mol^{-1} cm^{-1} and gives the fluorescence.

SEVERAL spectrophotometric and fluorimetric methods are described for the determination of aluminium. Generally, the methods are based on measuring the colour intensity formed by aluminium with the various lake forming reagents, such as alizarin-S, alizarin-S with calcium, aluminon, eriochrome cyanin-R *etc.*[1]. But these methods are not useful as the reactions are slow, and composition, consistency and reproducibility of colours are uncertain. Moreover, the methods are non-selective due to more interferences of diverse ions[1]. Pontachrome blue black R[2], hematoxylin[2] and morin[3] were also used for fluorimetric determination of aluminium. *N*-Phenylbenzohydroxamic acid (PBHA) along with 8-quinolinol in ammonium carbonate medium in presence of thioglycollic acid, hexametaphosphate, hydrogen peroxide and potassium cyanide as masking agents, was used for extraction and spectrophotometric determination of aluminium[4].

In the present investigation a method has been developed for the rapid extraction and spectrophotometric determination of aluminium(III) in ammonium carbonate medium with PBHA, and then forming an adduct type complex with morin. The aluminium-PBHA-morin complex is greenish yellow in colour and also gives fluorescence. Hence the aluminium is determined, in microgram quantities, spectrophotometrically and fluorimetrically.

Experimental

The spectrophotometric and fluorimetric measurements were made on Varian Superscan-3 spectrophotometer and Systronic 151 photofluorimeter, respectively.

All the chemicals used were of AnalaR and G.R. grades of B.D.H. or E. Merck respectively, unless otherwise specified. Synthesis of PBHA (m.p. 121°) has been described elsewhere[5]. The purity of freshly prepared reagent (PBHA) was checked by tlc, ir and uv spectra. A 0.5% (w/v) reagent solution was prepared in ethanol. Dilutions were made with ethanol whenever it was required. Morin 0.1% (w/v) solution was prepared in ethanol and dilutions were made whenever required. 20% (w/v) aqueous ammonium carbonate solution was used. Requisite amount of $AlCl_3.7H_2O$ was dissolved in distilled water. The final concentration of aluminium (III) solution was determined volumetrically[6].

An aliquot of standard aluminium solution (0-3 ppm) was made upto 5 ml with distilled water and to it added, solutions of ammonium carbonate (5 ml) and PBHA (1 ml) and mixed thoroughly. Then chloroform (10 ml) was added to the mixture and shaken for 3-4 min to extract aluminium-PBHA complex. The phases were allowed to separate and the organic layer alongwith chloroform washings (3×2 ml) transferred to a volumetric flask after drying over anhydrous sodium sulphate. To it was added morin solution (1 ml) and finally diluted to 25 ml with chloroform-alcohol mixture such as to maintain the solvents ratio 4 : 1 (v/v) in the final solution. The solution was warmed for 5 min on water bath at 55° for the colour development. The loss of volume due to warming was compensated by adding the solvent mixture.

The absorbance of the aluminium-PBHA-morin complex was measured at 430 nm against the reagent blank. The fluorescence intensity of aluminium-PBHA-morin complex solution was measured against the blank.

Results and Discussion

The aluminium-PBHA complex is colourless. The aluminium-PBHA-morin complex is greenish

yellow in colour having a maximum absorbance at 430 nm and gives the fluorescence.

Effect of pH and shaking time: The extractions were carried out at *p*H 7.0-9.0 and it was revealed that the maximum extraction is obtained at *p*H 8.0-8.8 (Table 1). 5 ml aliquot of ammonium carbonate solution gives the *p*H 8.8 which is most suitable for the extraction purpose. Complete extraction of aluminium-PBHA complex in chloroform was obtained by shaking for 3 min. The aqueous layer was tested for aluminium by alizarin-S[1] and indicated its absence.

TABLE 1—EFFECT OF *p*H ON THE EXTRACTION OF ALUMINIUM

Aluminium : 2.0 ppm, Solvent : Chloroform : EtOH (4 : 1), PBHA (0.5 % EtOH) : 1.0 ml, Morin (0.1 % EtOH) : 1.0 ml, λ_{max} : 430 nm

*p*H	Absorbance	E %	Molar absorptivity $l\ mol^{-1}\ cm^{-1}$
7.0	0.65	73	8.8×10^{3}
7.6	0.73	82	9.8×10^{3}
8.0	0.90	100	1.2×10^{4}
8.4	0.90	100	1.2×10^{4}
8.8	0.90	100	1.2×10^{4}
9.0	0.33	37	4.5×10^{3}

TABLE 2—EFFECT OF MORIN CONCENTRATION ON THE EXTRACTION OF ALUMINIUM

Aluminium : 2.0 ppm, *p*H : 8.8, PBHA (0.5 % EtOH) : 1.0 ml, Solvent : Chloroform : EtOH (4 : 1), λ_{max} : 430 nm, Morin : 0.1% in EtOH

Morin soln. ml	Absorbance	Molar absorptivity $l\ mol^{-1}\ cm^{-1}$
0.5	0.57	7.7×10^{3}
0.8	0.70	9.4×10^{3}
1.0	0.89	1.2×10^{4}
1.5	0.89	1.2×10^{4}
1.8	*	*
2.0	*	*

* Turbid.

TABLE 3—EFFECT OF THE SOLVENTS ON THE EXTRACTION OF ALUMINIUM

Aluminium : 2.0 ppm, *p*H : 8.8, PBHA (0.5% EtOH) : 1.0 ml Morin (0.1% EtOH) : 1.0 ml, Solvent : Chloroform—EtOH (4 : 1)

Solvent	λ_{max} nm	Molar absorptivity $l\ mol^{-1}\ cm^{-1}$	Fluorimeter reading (div.)
Chloroform	430	1.2×10^{4}	100
Benzene	436	1.0×10^{4}	60
MIBK	419	4.3×10^{3}	36
Isoamyl alcohol	*	*	*

* Complex not extractable.

Effect of reagent concentration: A study with varying concentration of PBHA at the optimum conditions reveals that a single extraction with 1 ml PBHA solution (0.5%) was enough for quantitative extraction. Lower reagent concentrations gave incomplete extractions. A study with varying concentrations of morin keeping PBHA concentration constant reveals that 1.0 ml morin solution (0.1%) gives the most satisfactory result (Table 2). The

TABLE 4—VALIDITY OF BEER'S LAW

Solvent : Chloroform : EtOH (4 : 1), Morin (0.1% EtOH): 1.0 ml, PBHA (0.5% EtOH) : 1.0 ml, λ_{max} : 430 nm, *p*H : 8.8

Aluminium ppm	Absorbance	Fluorimeter readings
0 02	0.009	2.5
0.05	0.023	6.2
0.10	0.045	12.5
0.20	0.090	25.0
0.40	0.180	50.0
0.60	0.270	75.0
0.80	0.360	100.0
1.00	0.450	–
1 20	0.540	–
1.40	0.630	–
1.60	0.720	–
2.00	0.900	–
2.40	1.080	–
3.00	1.350	–

TABLE 5—EFFECT OF DIVERSE IONS ON EXTRACTION OF ALUMINIUM

Aluminium : 2.0 ppm, *p*H : 8.8, PBHA (0.5% EtOH) : 1.0 ml Morin (0.1% EtOH) : 1.0 ml, Solvent : Chloroform : EtOH (4 : 1), λ_{max} : 430 nm, Absorbance : 0.90

Ions	Added as	Amount	Absorbance
Na^{+}	NaCl	50	0.90
K^{+}	KCl	50	0.90
Li^{+}	LiCl	50	0.90
Ca^{2+}	$CaCl_2$	50	0.90
Sr^{2+}	$SrSO_4$	50	0.90
Mg^{2+}	$MgCl_2$	50	0.90
Cu^{2+}	$CuSO_4$	50	0.91
Ni^{2+}	$NiCl_2$	50	0.89
Pb^{2+}	$Pb(NO_3)_2$	50	0.90
Fe^{3+}	$FeCl_3$	60	0.89
Bi^{3+}	$Bi(NO_3)_3$	50	0.89
Th^{4+}	$Th(NO_3)_4$	50	0.89
Sb^{3+}	Sb_2Cl_6	50	0.91
V^{5+}	VO_2Cl_2	50	0.90
Ba^{2+}	$BaCl_2$	100	0.91
Be^{2+}	$BeCl_2$	100	0.89
Cd^{2+}	$Cd(NO_3)_2$	100	0.90
Mn^{2+}	$MnSO_4$	100	0.90
Ce^{4+}	$Ce(SO_4)_2$	80	0.89
Sn^{4+}	$SnCl_4$	80	0.89
Cl^{-}	KCl	50	0.90
Br^{-}	KBr	50	0.90
I^{-}	KI	50	0.90
NO_3^{-}	KNO_3	50	0.90
SO_4^{2-}	K_2SO_4	50	0.89
BO_3^{3-}	Na_3BO_3	50	0.89
PO_4^{3-}	Na_3PO_4	50	0.89
CO_3^{2-}	Na_2CO_3	50	0.90

higher morin concentration gives turbidity and the lower one reduces the colour intensity.

Effect of solvents and stability: Amongst the several solvents chloroform, benzene, methyl isobutyl ketone (MIBK) and isoamyl alcohol, chloroform was found to be the most suitable solvent for extraction of aluminium (Table 3). The aluminium-PBHA-morin complex was found to show constant absorbance when a 4 : 1 ratio of chloroform ethanol mixture was taken. Further, the complete colour development takes 25 min but

on heating the complex to 55° this time is reduced to 5 min. The complexes were found to be stable for several days and absorbance was found to remain constant.

Beer's law: The aluminium as aluminium-PBHA-morin complex obeys the Beer's law within 0-3 ppm (Table 4) and the molar absorptivity was found to be 1.2×10^4 l mol^{-1} cm^{-1} at 430 nm. In the fluorimetric determination the Beer's law limits were found to be 0-0.8 ppm.

Effect of diverse ions: Table 5 shows the effect of various diverse ions for the determination of aluminium. The experiments were made on aqueous solutions containing 2.0 ppm of aluminium in presence of various amounts of diverse ions. Moderate amount of many ions commonly associated with aluminium can be tolerated.

References

1. E. B. SANDELL, "Colorimetric Determination of Traces of Metals", 3rd. ed., Interscience, New York, 1965.
2. H. W. KNUDSON, V. W. MELOCHE and C. JUDAY, *Ind. Eng. Chem. Anal. Ed.*, 1940, **12**, 715; W. D. HATFIELD, *Ind. Eng. Chem.*, 1924, **16**, 233; G. V. HOUGHTON, *Analyst*, 1943, **68**, 208; N. STRAFFORD, *Analyst*, 1943, **68**, 319; G. GINSBERG, *Angew. Chem.*, 1938, **51**, 663; M. ISHIBASHI, T. SHIGEMATSU and Y. NISHIKOWA, *Jpn. Analyst*, 1957, **6**, 568; J. L. STEENKAMP, *J. S. African Chem. Inst.*, 1930, 13, 64.
3. C. E. WHITE and C. S. LOWE, *Ind. Eng. Chem. Anal. Ed.*, 1940, **12**, 229; Z. G. SZABO and M. T. BECK, *Acta Chim. Acad. Sci. Hung.*, 1954, **4**, 211.
4. R. VILLFREAL JOHN, R. KRSUL and S. A. BARKER, *Anal. Chem*, 1969, **41**, 1420.
5. U. PRIYADARSHINI and S. G. TANDON, *J. Chem. Eng. Data*, 1967, **12**, 143.
6. "Vogel's Text Book of Quantitative Inorganic Analysis", eds. J. BASSETT, R. C. DENNY, G. H. JEFFERY and J. MENDHAM, 4th. ed., ELBS, London, 1978.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 617-618

Direct Gravimetric Determination of Copper(II) with a New Reagent, 3-(*o*-Carboxyphenyl)-1-*o*-tolyl-triazene-*N*-oxide

N. M. BANERJEE, B. C. RAY and S. LAHIRI*

Department of Chemistry, Jadavpur University, Calcutta-700 032

Manuscript received 20 June 1983, revised 24 February 1984, accepted 17 June 1984

3-(*o*-Carboxyphenyl)-1-*o*-tolyl-triazene-*N*-oxide has been used for the gravimetric determination of 2-30 mg Cu^{II}. The green complex, $Cu(C_{14}O_3N_3H_{11})$ is precipitated in the *p*H range 3-9 adjusted with aqueous caustic soda and hydrochloric acid, and is weighed as such after drying at 110-120°. Interferences caused by Zn^{II}, Cd^{II}, Mg^{II}, Ni^{II}, Co^{II}, Mn^{II}, Cr^{II}, Fe^{II}, Bi^{III}, Al^{III}, Pb^{II}, Sn^{II}, As^{III}, Sb^{III}, Mo^{VI}, W^{VI}, V^{V}, Nb^{V}, Ta^{V}, Rh^{II} and Os^{IV} could be overcome by adjustment of *p*H and by using tartrate as the masking agent, while the effects of Fe^{III} and Be^{II}, Hg^{II} and U^{IV} are removed by ammonium bifluoride, potassium iodide, and ammonium acetate, respectively. Tartrate does not interfere while the effect of oxalate, citrate, F^-, SCN^-, PO_4^{-3}, BO_3^{-3} and AsO_4^{-3} could be removed simply by the control of *p*H. The reagent has also been used in the determination of copper in alloys. The average relative error is ±0.50% and relative standard deviation is ±0.30.

A CRITICAL examination[1-5] of the important gravimetric methods for the determination of copper(II) with organic reagents indicates that the new reagent, 3-(*o*-carboxyphenyl)-1-*o*-tolyl-triazene-*N*-oxide, recommended in this communication for the gravimetric determination of copper(II) is one of the sensitive reagents for the metal ions. The reagent is selective for Cu^{II} at a suitable *p*H and/or in presence of masking agent. It reacts with Cu^{II} quantitatively at the *p*H range 3-9, forming greenish, thermally stable complex, $Cu(C_{14}O_3N_3H_{11})$. The procedure described is a simple one and consumes less time. The reagent has been successfully applied for the determination of copper in presence of diverse ions and in its alloys.

Experimental

Preparation of reagent: *o*-Nitrotoluene was reduced with Zn dust and NH_4Cl in aqueous solution (containing little alcohol) to *o*-tolylhydroxylamine. It was then coupled with diazotised anthranilic acid below 5°. The *p*H was raised to 5 by adding sodium acetate when a very light yellow precipitate was obtained. It was crystallised from ethanol to yield the reagent, m.p. 160° (Found: C, 62.18; H, 4.73; N, 15.68. Calcd. C, 61.98; H, 4.83; N, 15.49%).

Copper(II) solution: Electrolytically pure copper was dissolved in nitric acid and to this was added concentrated sulphuric acid (3-4 ml) and the solution evaporated until white fumes evolved. The metal content was determined in the usual way[6]. A Systronics *p*H meter was used to control the *p*H values.

General procedure: To an aliquot of standard solution of copper (2-30 mg Cu) was added a solution of sodium potassium tartrate (10 ml, 10%). Tartrate was not needed below *p*H 4.5. It was diluted to 150-200 ml and the *p*H adjusted to 3-9 with aqueous caustic soda and hydrochloric acid. The mixture was heated on water bath and a hot ethanolic solution of the reagent (0.05-0.25 gm) was added with constant stirring. The precipitate formed was digested on water bath for 20-30 min with occasional stirring. The greenish complex was then filtered hot through Gooch crucible (no. 3), washed several times with hot distilled water and dried at 110-120° to constant weight. The results of several determinations of Cu^{II} are presented in Table 1.

TABLE 1—DETERMINATION OF Cu^{II} WITH 3-(*o*-CARBOXYPHENYL)-1-*o*-TOLYL-TRIAZENE-*N*-OXIDE

Cu taken mg	Weight of complex mg		Cu found mg		Relative error %	
2.06	10.85	10.87	2.07	2.075	+0.53	+0.73
8.84	46.00	46.21	8.78	8.82	−0.72	−0.27
29.48	153.65	154.80	29.33	29.55	−0.51	+0.24

Procedure in presence of diverse ions: A known volume of Cu^{II} and foreign cation or anion, and 1.0-1.5 gm of suitable masking agent, where necessary, were diluted to 200 ml. The *p*H of the mixture was adjusted around 4.0, Cu^{II} was then determined as described under general procedure. Table 2 records the results.

Determination of Cu^{II} in alloys: Accurately weighed standard alloy (200 mg) was dissolved

in dil. nitric acid and evaporated slowly with conc. H_2SO_4 (3-4 ml) until the evolution of dense fumes of sulphur trioxide ceased. The content were cooled, filtered in a 100 ml volumetric flask and the volume made upto the mark. The determination of Cu^{II} was then carried out with the prepared solution in the usual way. The results are recorded in Table 3.

TABLE 2—SEPARATION OF Cu^{II} FROM DIVERSE IONS
Cu taken : 8.84 mg

Diverse ions added mg	Masking agent	Weight of complex mg	Cu found mg	Relative error %
Oxalate (100)	–	46.0	8.78	– 0.68
Citrate (100)	–	46.50	8.88	+ 0.45
Tartrate (1,500)	–	46.48	8.87	+ 0.34
Fluoride (500)	–	46.21	8.82	– 0.23
Thiocyanate (200)	–	46.38	8.85	+ 0.11
Phosphate (100)	–	46.44	8.86	+ 0.23
Borate (100)	–	46.28	8.83	– 0.11
Arsenate (100)	–	46.15	8.81	– 0.34
Zn^{2+} (50)	Na-K-tartrate	46.48	8.87	+ 0.34
Cd^{2+} (50)	,,	46.50	8.88	+ 0.45
Mg^{2+} (200)	,,	46.10	8.80	– 0.45
Al^{3+} (50)	,,	46.44	8.86	+ 0.23
Bi^{3+} (50)	,,	46.46	8.87	+ 0.34
As^{3+} (50)	,,	46.36	8.85	+ 0.11
Sb^{3+} (50)	,,	46.52	8.88	+ 0.45
MoO_4^{2-} (50)	,,	46.21	8.82	– 0.23
WO_4^{2-} (50)	,,	46.54	8.88	+ 0.45
Pb^{2+} (50)	,,	46.36	8.85	+ 0.11
Mn^{2+} (30)	,,	46.48	8.87	+ 0.34
Ni^{2+} (30)	,,	46.28	8.83	– 0.11
Co^{2+} (30)	,,	46.48	8.87	+ 0.34
Ta^{5+} (50)	,,	46.38	8.85	+ 0.11
Nb^{5+} (50)	,,	46.21	8.82	– 0.23
Rh^{3+} (50)	,,	46.44	8.86	+ 0.23
Os^{4+} (50)	,,	46.48	8.87	+ 0.34
UO_2^{2+} (50)	Ammonium acetate	46.36	8.85	+ 0.11
Fe^{3+} (50)	NH_4HF_2	46.44	8.86	+ 0.23
Be^{2+} (200)	,,	46.28	8.83	– 0.11
Hg^{2+} (50)	KI	46.21	8.82	– 0.23

TABLE 3—DETERMINATION OF Cu^{II} IN ALLOYS

Samples	Copper certified	Copper found
Tin bronze	77.69%	77.88%
Aluminium bronze	85.90%	85.83%
Brass	67.40%	67.31%
Manganese bronze	57.20%	57.29%

Results and Discussion

Effect of pH *and reagent concentration :* A set of experiments was carried out under stated conditions but with variation of pH. It was observed that the precipitation of copper complex commenced at pH 2 and was quantitative between pH 3.0 and 9.0. In another series of experiments the pH was fixed around 6.0 and the amount of the reagent was varied. It was found that 1.5 times the theoretical quantity of the reagent was sufficient for complete precipitation and excess reagent (upto 5 fold excess) showed no adverse effect on the determination. The precipitation was not quantitative below pH 3.0 and above pH 9.0.

Properties, composition of the complex : The copper complex with 3-(*o*-carboxyphenyl)-1-*o*-tolyltriazene-*N*-oxide melts at 262°(d). The complex is sparingly soluble in water and in 20% ethanol but soluble in absolute ethanol. The complex was analysed for copper by iodometric method and nitrogen by Dumas method. (Found : Cu, 19.07 ; N, 13.0. $Cu(C_{14}O_3N_3H_{11})$ calcd. Cu, 19.09 ; N, 12.62%). The ir band at 3235 cm^{-1} (N-H stretch), and 1665 and 1264 cm^{-1} (-COOH and N-O stretches) in free ligand disappear and shift to lower frequencies, respectively in the complex. This indicates that chelation takes place through N-H and COOH by proton displacement and through O of N-O with the formation of M-O bond. The absence of band for water in the complex spectra suggests that it has apparently a tri-coordinated structure and is probably dimeric one where *N*-oxide oxygen or the carboxyl oxygen acting as the bridging atom.

Interferences : The determination of Cu^{II} was not possible in the presence of disodium EDTA and cyanide while large excess of citrate, oxalate, thiocyanate and phosphate masked Cu^{II} partially.

Precision and accuracy : The average relative error in the determination of Cu^{II} by the procedure described is $\pm 0.50\%$ and the relative standard deviation ± 0.30.

References

1. S. C. SHOME, *Analyst*, 1950, 75, 27.
2. L. SILVERMAN, *Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 343.
3. P. WENGER and Z. BESSO, *Mikrochim. Acta*, 1941, **29**, 240.
4. L. DUCRET, *Bull. Soc. Chim. Fr.*, 1945, **12**, 880.
5. S. C. SAHA, D. CHAKRABARTY and P. K. CHAKRABARTY, *Indian J. Chem., Sect. A*, 1977, **15**, 816.
6. B. C. BHATTACHARYA and B. C. RAY, *Indian J. Chem.*, 1975, **13**, 1066.
7. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", 3rd. ed., Longmans, London, 1963, p. 358.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 619-620

Ultrasonic Studies for the Micro Estimation of Lead(II) with Diethyldithiocarbamate

(MISS) SUNITA PRADHAN*, B. K. MAHESHWARI and R. L. YADAV

Chemical Laboratory, Holkar Science College, Indore

Manuscript received 27 December 1982, revised 5 October 1983, accepted 3 May 1984

Ultrasonic velocity measurements to an accuracy of ±0.05% have been determined in the micro estimation of lead(II) using sodium diethyldithiocarbamate as reagent at 25°. The adiabatic compressibilities calculated yielded results of quantitative significance.

IN recent years sodium diethyldithiocarbamate (NaDDC) has been used for gravimetric and volumetric estimations[1-3] of many metal ions. No ultrasonic studies involving the compound, however, has been reported in the literature.

The present investigation is therefore initiated to estimate lead(II) on microscale with NaDDC by ultrasonic velocity and adiabatic compressibility measurements.

Experimental

All chemicals used were of analaR grade. Triple distilled water was used throughout. The solution of NaDDC was prepared fresh. The solutions of metal ions and NaDDC of desired strengths were prepared from the concentrated stock solutions. Lead diethyldithiocarbamate in sufficiently dilute solution was not found to precipitate.

The investigations were made at 25° by circulating thermostated water around the measuring cell. Ultrasonic velocity was determined using a single crystal variable path interferometer, working at 1 MHz and capable of yielding a velocity measurement to an accuracy of ±0.05%. The measuring cell containing 5 ml solution of metal salt was connected to the out-put terminal of the high frequency generator. The micrometer was slowly moved till the anode current on the meter on high frequency generator showed a maximum. A number of maxima readings of the anode were passed and their number, n was counted. The total distance, d moved by the micrometer gave the value of the wavelength, λ with the help of the following equation

$$d = n\,\lambda/2$$

Once the λ is known the velocity, v in the liquid can be easily calculated with the help of the relation

$v = \lambda F$, where F is the frequency.

The procedure was repeated after the addition of 0.5 ml NaDDC each time. The results are recorded in Table 1.

TABLE 1

10^4[NaDDC] = 4.0 *N*; 10^4[Lead nitrate] = 2.0 *N*
Temp. = 25°; Vol. of lead nitrate solution = 5.0 ml

Observed end point	2.48 ml
Calculated end point	2.50 ml
Metal ions found	0.412 µg
Metal ions calculated	0.414 µg

A bicapillary pyknometer and an accurate analytical balance with an accuracy of 0.0001 gm were used for the determination of density and micro-burette was used for the addition of NaDDC solution. The adiabatic compressibility, β of the solution was calculated by Newton and Laplace equation[4].

$$\beta = 1/\varrho v^2$$

where v and ϱ are the ultrasonic velocity and density of the solution, respectively.

Results and Discussion

In aqueous solutions of metal salt, the ultrasonic velocity generally increases with increasing concentration of the salt, whereas the adiabatic compressibility decreases with increase of concentration. Abnormal behaviour in solutions of lead nitrate of course has been reported[5-7].

In the present investigation the ultrasonic velocity of metal salt solution was first found to decrease on addition of NaDDC and then increased, and β of the salt solution on addition of NaDDC was first found to increase and then decreased.

Fig. 1 depicts changes of ultrasonic velocity and β due to addition of NaDDC to metal ions. The

curves show negative and positive deviation from linearity in ultrasonic velocity and β, respectively.

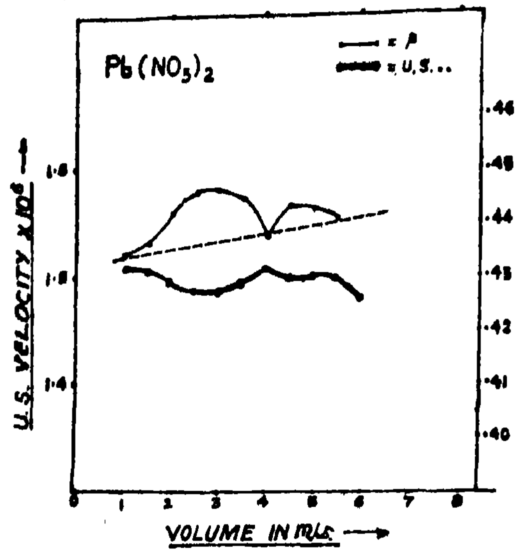


Fig 1.

The ultrasonic velocity is dependent on many factors like intra-molecular forces[8], non ideality

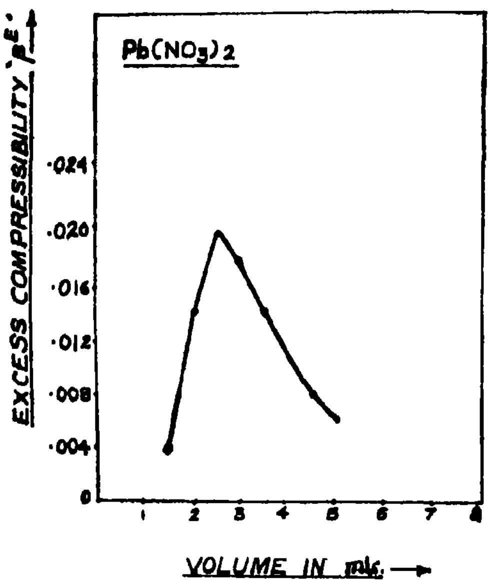


Fig 2.

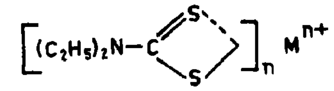
in free length[9] and interaction due to ion-association or chelation. The ion-association in the case of NaDDC and many metal ions are reported in the literature. The advantage of ion-association of lead(II) and NaDDC are taken for the micro estimation of metal ions by ultrasonic velocity and β measurements.

The values of excess compressibility[10], β^E, with the addition of NaDDC are depicted in Fig. 2.

Since the excess of compressibility is a measure of the extent of deviation from ideal behaviour, it is also a measure of the extent of interaction due to ion-association or chelation between NaDDC and metallic ions. The maximum deviation is a stage which shows the completion of the derivative formation. The end point is well marked in Fig. 1 and 2. The results are summarised in Table I.

The experimental observations were found to be in excellent agreement with the calculated results, and reproducible within $\pm$ 0.05%.

NaDDC forms water insoluble complex salt of the type



where M is the metal and n its valency. These compounds were found to be soluble in organic solvents, such as chloroform, ether and acetone.

References

1. V. Sedivec and V. Vasak, *Listy (Czech.)*, 1949, **43**, 269.
2. W. Reinhold, *Z. Anal. Chem.*, 1956, **152**, 259.
3. C. O'Connor, J. D. Gulbert and G. Wilkinson, *J. Chem. Soc. A*, 1969, 84.
4. R. T. Beyer and S. V. Letcher, "Physical Ultrasonics", Academic Press, New York, 1969.
5. A. Giacomini and Posce, *Ricerca Sci.*, 1940, **2**, 605.
6. R. Barthel, *J. Acoust. Soc. Am.*, 1954, **26**, 227.
7. B. H. Krishnamurty and M. S. Murty, *J. Sci. Ind. Res.*, 1958, **17B**, 216.
8. M. V. Kaulgud, *Acoustic*, 1960, **10**, 316 (*Chem. Abstr.*, 1961, **55**, 19395).
9. A. Weissberger, "Technique of Organic Chemistry", Interscience, New York, 1965, Vol. 4.
10. T. Satyavati, P. J. Reddy and S. V. Subramanyam, *J. Phys. Soc. Jpn.*, 1962, **17**, 1061.

J. Indian Chem. Soc.,
Vol. LXI, July 1984, pp. 621-623

Extraction and Spectrophotometric Determination of Cobalt with Substituted Pyridines and Thiocyanate

PARTHA CHATTOPADHYAY and SANTOSH K. MAJUMDAR

Department of Chemistry, University of North Bengal, Darjeeling-734 430

Manuscript received 16 July 1982, revised 23 November 1983, accepted 26 May 1984

Cobalt(II) forms complexes with α-picoline/β-picoline/γ-picoline/2 : 4 : 6-collidine in thiocyanate system. These complexes are readily extractable into ethylacetate. All species absorb sharply at 620 nm. The colour of the extracts is extremely stable and can be directly measured spectrophotometrically. The sensitivities are 0.040, 0.040, 0.045, 0.035μg cm⁻² Co^{II} and molar absorptivities are 1.415×10^3, 1.485×10^3, 1.375×10^3 and 1.721×10^3 l mol⁻¹ cm⁻¹ for α-pic., β-pic., γ-pic. and 2 : 4 : 6-collidine, respectively. A quick and very simple method has been proposed for determination of microgram amounts of cobalt in presence of copper and iron and other metal ions.

THE studies on the extraction and other chemical behaviour of the pyridine thiocyanate complex of cobalt is known in the literature[1-3], but the extraction studies with different substituted pyridines in presence of thiocyanate are not reported. Under suitable conditions, cobalt forms pyridine thiocyanate complex readily. The structure for the cobalt complex has been given[1] as $CoPy_4(SCN)_2$. The conditions under which this compound forms was examined and a procedure was described for the separation of cobalt and nickel as pyridine thiocyanate using solvent extraction by methyl isobutyl ketone[4]. In the present communication, we report the results of our studies on the extraction behaviour of cobalt(II) with α-picoline, β-picoline, γ-picoline and 2 : 4 : 6-collidine in thiocyanate system using ethyl acetate. Based on these studies, a rapid and sensitive method for the extraction and spectrophotometric determination of trace amounts of cobalt(II) has been developed.

Experimental

Absorbance measurements were carried out with a Beckman DU2 spectrophotometer with optically matched quartz cells (1 cm). ECL 5651 digital *p*H meter was used for *p*H measurements. Ethyl acetate (E. Merck), α-picoline (Riedel), β-picoline (BDH), γ-picoline (Fluka) and 2 : 4 : 6-collidine (BDH) were distilled before use. Ammonium thiocyanate (BDH) solution (30%, w/v) was prepared in double-distilled water. All other chemicals were either chemically pure or analytical reagent grade. A stock solution of cobalt sulphate was standardized by EDTA using xylenol orange indicator[5]. Solutions of appropriate concentrations were prepared by dilution.

An aliquot containing 100-800 μg of cobalt was transferred to a 50 ml separatory funnel and water added as necessary to give a total volume of 5 ml. Ammonium thiocyanate (1 ml), dil. HCl (2 ml, ~2*N*) and α-pic./β-pic./γ-pic./2 : 4 : 6 collidine (1 ml) were added by swirling and finally the volume was made to 10 ml by adding water. 20 ml of ethyl acetate was added and the mixture was equilibrated by shaking for 2 min. After phase separation, lower aqueous phase was drained out and ethyl acetate layer collected in 25 ml volumetric flask and diluted to the mark by excess solvent. The absorbance of the sample solution was measured against a reagent blank at 620 nm. Amount of cobalt extracted was finally computed from a previously prepared calibration curve.

Results and Discussion

Absorption curves : The spectral curves of the Co^{II} picolines thiocyanate complexes in ethyl acetate over the spectral range 550-700 nm are shown in Fig. 1. The reagents absorb quite insignificantly over this spectral range. In each case the distinctive peak at 620 nm was chosen for analytical measurements. The tail of the peak of each complex becomes a shoulder near 580 nm.

Effect of acidity : In each case the percentage of metal ion extracted was studied as a function of *p*H by varying hydrochloric acid concentration. In α-pic.-SCN and 2 : 4 : 6-collidine-SCN system a broad *p*H range was found where complete extraction of the metal is possible. In Fig. 2, extent of extraction of cobalt complex as a function of *p*H is shown by a composite diagram.

Calibration curve : Different amounts of cobalt were extracted, as described in the general procedure, at the corresponding *p*H and the absorbances were measured. In all the cases reagent blanks were prepared. The aqueous phase after each extraction was clear and colourless. The Beer's

law ranges for the amount of $\mu g\ ml^{-1}$ Co^{II} ethyl acetate in α-pic.-SCN, β-pic.-SCN, γ-pic.-SCN, and 2 : 4 : 6-collidine-SCN are 4-40, 4-40, 4.5-45, and 3.5-35, respectively.

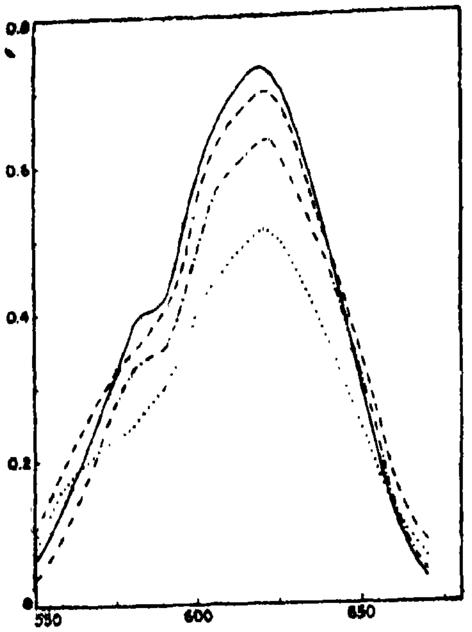


Fig. 1. Absorption spectrum of cobalt complex. — 2 : 4 : 6-collidine-SCN, - - - γ-pic.-SCN, -.-.- β-pic.-SCN, ... α-pic.-SCN.

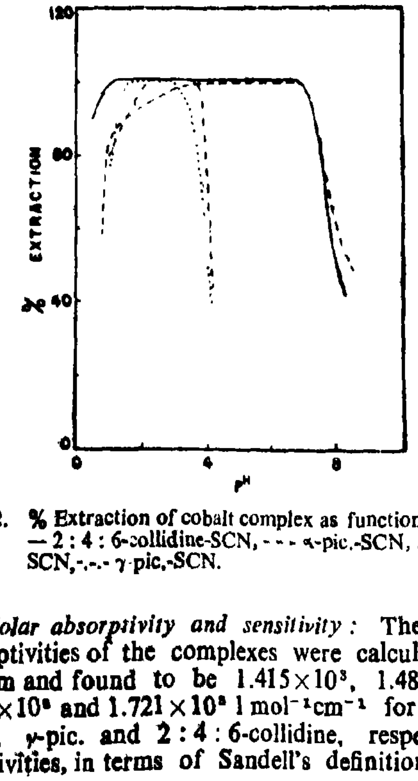


Fig. 2. % Extraction of cobalt complex as function of pH. — 2 : 4 : 6-collidine-SCN, - - - α-pic.-SCN, ...β-pic.-SCN, -.-.- γ-pic.-SCN.

Molar absorptivity and sensitivity : The molar absorptivities of the complexes were calculated at 620 nm and found to be 1.415×10^3, 1.485×10^3, 1.375×10^3 and 1.721×10^3 $l\ mol^{-1}cm^{-1}$ for α-pic., β-pic., γ-pic. and 2 : 4 : 6-collidine, respectively. Sensitivities, in terms of Sandell's definition[6], are 0.040, 0.040, 0.045 and 0.035 $\mu g\ Co^{II}\ cm^{-2}$, respectively. In methyl isobutyl ketone, sensitivity[4] of $Co(Py)_4(SCN)_2$ is 0.02 $\mu g\ Co^{II}\ cm^{-2}$. Thus it may be concluded that for relatively lower cobalt concentration pyridine itself has some advantage over its substituted analogues.

Effect of reagents concentration : Variation of reagent concentration was tested at the corresponding pH keeping the other variables same. It was found that 1 ml of the respective reagents and 1 ml aqueous ammonium thiocyanate (25%, w/v) are sufficient to extract 1000 μg of Co^{II}. Amount of organic reagents below 1 ml and aqueous thiocyanate (25%) below 1 ml resulted in incomplete extraction. Higher concentrations (1 ml for 100% organic reagents and 1 ml for 25% aq. thiocyanate) had no effect on extraction and was avoided because of reagent economy.

Extraction time : The absorbance of Co^{II} picolines-thiocyanate in ethyl acetate was tested as a function of extraction time. The absorbance was essentially constant for the extraction time range 1.5-3 min.

Stability of colour of the extract : The absorbance values of ethyl acetate extract containing 200-1000 μg Co^{II} were measured at different intervals of time. The colour of the complexes in the organic phase was found to be stable even after seven days.

Efficiency of extraction : The extent of extraction was investigated quantitatively by developing the colour of Co^{II} in the aqueous phase after extraction by the recommended procedure. Excess thiocyanate of the aqueous phase was destroyed and cobalt content was determined by 2,2'-pyridyl monooxime method[7]. An average 3 μg of cobalt was detected in the aqueous phase after extraction of three separate solutions containing 500 μg cobalt. Considering the reliability of this method, more than 99.4% of the cobalt is extracted.

Effect of foreign ions : The selectivity of the recommended procedure was investigated by the determination of 20 $\mu g\ ml^{-1}$ of cobalt in the presence of a number of other ions. An ion was considered to interfere if the absorbance obtained differed by more than ±2% from that for cobalt alone. The following metal (M) ions, added as chloride, nitrate or sulphate cause no interference at the Co : M weight ratio given, $Be\geqslant200$, $Mg^{II}\geqslant150$, $Ca^{II}\geqslant100$, $Sr^{II}\geqslant100$, $Ba^{II}\geqslant100$, $Zn^{II}\geqslant100$, $Cd^{II}\leqslant75$, $Hg^{II}\leqslant50$, $La^{II}\leqslant400$, $Al^{III}\geqslant300$, $Ni^{II}\leqslant10$, $Pd^{II}\leqslant5$, $Pt^{IV}\leqslant10$, $Rh^{III}\leqslant20$, $Zr^{IV}\leqslant100$, $U^{VI}\leqslant100$, $Th^{IV}\geqslant100$, $Mn^{II}\geqslant150$, $Fe^{III}\leqslant100$, $Cu^{II}\leqslant8$ and alkali metals $\geqslant500$. Among anions, phosphate, acetate, fluoride, tartrate, borate, molybdate, bromide, iodide, thiosulphate (added as alkali metal salts) do not interfere even when their weight is at least 300 times than that of cobalt. Tolerance limit of oxalate and citrate ions are quite low. Only 1.5 mg oxalate

ion and 2.0 mg citrate ion permit quantitative extraction of 20 $\mu g\ ml^{-1}$ Co, while trace amount of EDTA prevents cobalt from extracting quantitatively to the organic phase. An excess amount of tartrate ion aptly removes the interference of Fe^{III}. A sufficiently large excess of thiosulphate ion prevents Cu^{II} from co-extracting to the organic phase. Tolerance limits of Pd^{II}, Pt^{IV}, Rh^{III} and Ni^{II} could not be improved either by adding excess reagents or by using common masking agents. In the presence of Pd^{II}, Pt^{IV} and U^{VI} the organic extract turns green. This is probably due to co-extraction of these metals with cobalt to the organic layer. However, in the presence of the amount indicated earlier for these three metal ions cobalt complex offers a steady absorbance value as expected for its own.

Determination of Co^{II} in synthetic mixtures : Following three mixtures were prepared and cobalt content of each of these mixtures was determined by the recommended procedure.

Mixture (i) : 0.5 mg Co^{II} + 50 mg Fe^{III} + 15 mg Ni^{II} per 5 ml.

Mixture (ii) : 0.5 mg Co^{II} + 15 mg Cu^{II} + 15 mg Ni^{II} per 5 ml.

Mixture (iii) : 0.5 mg Co^{II} + 50 mg Mn^{II} + 50 mg Fe^{III} per 5 ml.

For mixtures (i) and (iii) an excess amount of tartrate ion and for mixture (ii) an excess of thiosulphate ion was added prior to addition of the reagents. All the three mixtures offered quite satisfactory results with α-pic./β-pic./γ-pic., 2 ; 4 : 6 collidine, and thiocyanate.

Acknowledgement

The authors are thankful to U.G.C., New Delhi, for the award of a research fellowship (P.C.) and to the Head of the Chemistry Department for necessary facilities.

References

1. R. Z. Reitzenstein, *Z. Anorg. Chem.*, 1898, **18**, 253 ; 1902, **32**, 304.
2. H. Grossman, *Chem. Ber.*, 1904, **37**, 559.
3. T. L. Davis and H. R. Batchelder, *J. Am. Chem. Soc.*, 1930, **52**, 4069.
4. J. H. W. Forsythe, R. J. Magee and C. L. Wilson, *Talanta*, 1958, **1**, 249.
5. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", ELBS, London, 1962, p. 443.
6. E. B. Sandell, "Colorimetric Determination of Traces of Metals", Intersciences, New York, 1959, p. 83.
7. S. Stupavsky and W. J. Halland, *Mikrochim. Acta*, 1970, **1**, 115.

Notes

Conductometric and Spectrophotometric Studies on Scandium(III), Yttrium(III) and Lanthanum(III) Complexes with Violuric Acid

R. M. AWADALLAH, M. K. SHERIF and A. A. M. GAD

Chemistry Department, Faculty of Science, Aswan, A. R. Egypt

Manuscript received 16 December 1980, revised 7 October 1983, accepted 3 May 1984

VIOLURIC acid (5-oximinobarbituric acid) is of great use as a good organic chelating agent and a metal indicator for the analytical determination of minute amounts of transition metals. It was introduced as an indicator[1] for the complexometric titration of copper with complexon II. It is also used for the gravimetric microdetermination of palladium[2], for the photometric determination of copper[3], and for the spectrophotometric studies[4] of its V^V, Nb^V and Ta^V complexes. Sc^{III} and La^{III} chelates with alizarin red S and quinizarin sulphonic acid were studied spectrophotometrically and conductometrically[5]. Scandium was also studied spectrophotometrically using xylenol orange as a complexing agent[6,7].

Experimental

Solutions ($10^{-3}M$) of Sc^{III}, Y^{III} or La^{III} were prepared[8,9] by dissolving appropriate quantities of the A.R. grade (99.9%) $Sc(NO_3)_3.4H_2O$, $Y_2(SO_4)_3$ and $La(NO_3)_3.6H_2O$ in double distilled water. Violuric acid solution ($10^{-2}M$) was prepared by dissolving the requisite amount of reagent in double distilled water. Oxalic, boric, succinic acids, Na_2SO_4, $Na_2B_4O_7.10H_2O$ and Na_2CO_3 buffers of *p*H 1.83-11.31 were prepared[10] and standardised using *p*H meter.

Uv spectra was recorded on Pye Unicam SP 8000 spectrophotometer, using 1 cm silica cell. Pye Unicam model 290 MK 2 *p*H meter and Solu. Bridge, REG. U.S. PAT. OFF. Soil Tester, RD B15 Ser. 34621 were used.

Procedure: The conductometric titrations were carried out by titrating a known volume (V_1) of the metal ions with 0.5 ml increments of violuric acid (VA) (V_2), then measuring the specific conductivity after 2 min stirring and correcting the conductance due to dilution effect. Conductometric measurements were made using constant concentration of the metal ions and variable concentration of VA keeping the total volume constant, then thermostating the solutions at 30° for 2 h. The spectrophotometric measurements were performed at 200-300 nm. The reference solution was prepared by mixing the metal ion with the ligand-buffer mixture using a blank solution containing the same [VA] in the same buffer as in the test solution of the metal ion.

Results and Discussion

Conductance values obtained during the titration of Sc^{III}, Y^{III} and La^{III} increase with the increase of [VA]. Increase of conductance may be as a result of the liberation of H^+ ions from violuric acid which increase the conducting power of the solution leading to complex formation[11,12].

The spectrograms of Sc^{III}-, Y^{III}- and La^{III}-violurates are characterised by one peak. The spectral absorbance of the complexes is influenced by the following factors.

(i) *Effect of* pH: The spectral absorbance of the solutions of the complexes were measured at 200-300 nm using a series of buffer solutions (*p*H 1.83-11.31). The absorbance of the solutions of complexes increased with increasing *p*H reaching the maximum development of complex formation at *p*H 9.83 for Sc^{III} (λ_{max}=228 nm), 7.7 for Y^{III} (λ_{max}=240 nm) and 8.83 for La^{III} complex (λ_{max} =235 nm), and then slowed down. Observation of different bands may be due to the progressive formation of different convertible species of complexes. Shift to longer wavelength may be attributed to the formation of complexes absorbing lesser amounts of energy than those appearing at shorter wavelengths (absorbing large amounts of energy). Shift to shorter wavelength may be due to a shift in ionisation which denotes that the π-π^* transitions within the heterocyclic ring are influenced by inter- and intra-molecular charge transfer.

(ii) *Effect of ligand concentration*: The concentrations of Sc^{III} and La^{III} ($5\times10^{-5}M$) and Y^{III} ($10^{-4}M$) was kept constant, and [VA] changed in the range 10^{-5}-$2.5\times10^{-4}M$ in the case of Sc^{III} and La^{III} and 2×10^{-5}-$6\times10^{-4}M$ in the case of Y^{III} complexes. The spectral absorbance increased gradually with the increase of [VA] due to gradual complex formation having large ligand concentration, then approached a limiting value. As [VA] increases, λ_{max} shifts to longer wavelengths as a result of an intramolecular charge transfer and a π-π^* transition through the heterocyclic system.

(iii) *Effect of metal ion concentration*: The [VA] was held constant at $1\times10^{-4}M$ in the case of Sc^{III} and La^{III}, and $2\times10^{-4}M$ in the case of Y^{III}, whereas the concentration of Sc^{III} and La^{III} was changed from 5×10^{-6} to $1.8\times10^{-4}M$ and that of Y^{III} from 1×10^{-5} to $4\times10^{-4}M$. The absorbance of the solutions increased apparently.

Beer's law is valid for the microanalytical determination of 2.25 ppm Sc ($\varepsilon=8\times10^3$mol^{-1}cm^{-1}), 8.89 ppm Y ($\varepsilon=1.9\times10^4$mol^{-1}cm^{-1}) and 11.11 ppm La ($\varepsilon=7.5\times10^3$mol^{-1} cm^{-1}).

TABLE 1—EVALUATION OF STOICHIOMETRY, CONDITIONAL STABILITY CONSTANT (K_f) AND FREE ENERGY ($\Delta°G$ IN kcal mol^{-1} AT 25°) OF Sc^{III}-, Y^{III}- AND La^{III}- VIOLURATE COMPLEXES

Method	Ratio	Sc^{III}-violurate		Y^{III}-violurate		La^{III}-violurate	
		K_f	$\Delta°G$	K_f	$\Delta°G$	K_f	$\Delta°G$
M.R.	1 : 1			0.095×10^{7}	8.203	13.636×10^{11}	16.653
	1 : 2	0.21×10^{13}	16.927			1.56×10^{15}	20.85
	1 : 3	4.97×10^{18}	25.658	0.53×10^{17}	22.952	0.252×10^{17}	22.404
	1 : 4	0.292×10^{20}	26.713	11.53×10^{20}	28.904		
C.V.	2 : 1	0.148×10^{6}	7.095				
	1 : 1	0.803×10^{8}	10.276	0.03×10^{8}	8.888	0.45×10^{8}	10.503
	1 : 2	1.254×10^{12}	16.602	0.155×10^{12}	15.357	9.932×10^{12}	17.836
	1 : 4	0.345×10^{20}	268.19	3.56×10^{20}	28.204	2.141×10^{22}	30.645
S.L.	1 : 1	2.63×10^{10}	14.30	19.395×10^{12}	18.225	0.12×10^{8}	9.715
	1 : 2	1.022×10^{16}	21.97			10.74×10^{17}	24.745
L.L.	1 : 1	0.049×10^{7}	7.809	0.02×10^{4}	3.158	0.018×10^{4}	3.095
pH	1 : 1	0.267×10^{8}	10.192	0.138×10^{6}	7.054	0.135×10^{7}	8.413

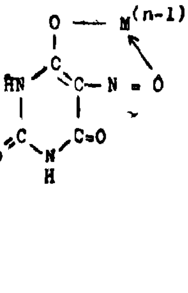
Stoichiometry of the complexes: The composition of Sc^{III}, Y^{III} and La^{III} complexes was determined from conductometric titrations, conductometric measurements and spectrophotometric methods (molar ratio, M.R.[18]; continuous variation, C.V.[14,15]; straight line, S.L.[16]; and limiting logararithmic, L.L.[18] methods). The results obtained are recorded in Table 1.

The conditional formation constant: The conditional stability constants of the complexes were evaluated making use of the results of the spectrophotometric methods[13-18] and the analytical (A-pH) method[19]. The free energy change ($\Delta°G$) of the complexes was calculated using the relation

$$\Delta°G = -RT \ln k.$$

The results of stoichiometry, stability constant and free energy of the complexes are presented in Table 1. The data indicate that the stability of the complexes are in the order La^{III}->Y^{III}->Sc^{III}-violurates.

The complexation takes place through covalent linkage between the central metal ion and the C-OH group, and coordination between the central metal ion and the nitroso group[20]. Complexation through covalent linkage is confirmed from the results of the conductivity experiments. The results show an increase in conductance values with the increase of [VA] as a result of increasing conducting power of the solutions containing ionic species (H^+ ions) liberated due to dissociation of the ligand which manifests the gradual increase of the molar conductivity of the solution. The mobility of the hydrogen ions liberated, moves faster and gather enhanced electrical field and thus increases the conductivity of the solution. Linkage between violuric acid and the metal ions in the complexes (1 : 1) can be typified as follows :



References

1. P. P. SOLODOVNIKOV, *Zh. Anal. Khim.*, 1963, **18**, 1026.
2. M. ZIEGLER and O. CLEMSER, *Mikrochim. Acta*, 1956, 1515.
3. M. ZIEGLER, *Z. Anal. Chem.*, 1958, **164**, 387.
4. R. M. AWADALLAH, *J. Indian Chem. Soc.*, 1980, **57**, 685.
5. I. M. ISSA, R. M. ISSA, A. M. HAMMAM and K. A. IDRIS, *Egypt. J. Chem.*, 1974, **17**, 911
6. A. I. CHERKESOV and N. M. ALYKOV, *Zh. Anal. Khim.*, 1965, **20**, 202.
7. H. T. BESCHETNOVA, *Sb. Nauch. Soobshch. Eagastan. Zh. Khim.*, 1972, 15022.
8. N. H. FERMAN, "Standard Methods of Chemical Analysis", 6th ed., Van Nostrand, New York, 1966.
9. J. ROSIN, "Reagent Chemicals and Standards", 5th ed., Van Nostrand, New York, 1967.
10. H. T. S. BRITTON, "Hydrogen Ions", 4th ed., Van Nostrand, New York, Vol. 1, 1956.
11. R. M. ISSA, M. S. MASSOUD and S. E. ZAYAN, *Egypt. J. Chem.*, 1969, **12**, 309.
12. E. M. KHAIRY, A. E. MAHGOUB and I. M. KENAWI, *Egypt. J. Chem.*, 1974, **17**, 811.
13. J. H. YOE and M. M JONES, *Ind. Eng. Chem. Anal. Ed.*, 1944, **16**, 111.
14. P. JOB and C. R. HEBD, *Seances Acad. Sci.*, 1925, **180**, 928.
15. F. G. SCHERIEF and A. M. AWAD, *J. Inorg. Nucl. Chem.*, 1962, **24**, 149.
16. E. I. ASMUS, *Z. Anal. Chem.*, 1960, **178**, 104.
17. A. E. HARVEY and D. L. MANNING, *J. Am. Chem. Soc.*, 1950, **72**, 4488.
18. H. E. BENT and C. L. FRENCH, *J. Am. Chem. Soc.*, 1941, **63**, 568.
19. R. M. AWADALLAH, M.Sc. Thesis, Assiut University, 1971.
20. R. M. AWADALLAH, *Aust. J. Chem.*, submitted for publication.

Spectral Studies on Bis-(β-Naphthylidine-*o*-amino phenolato) Chelates of Cerium(III), Samarium(III), Gadolinium(III), Dysprosium(III), Cobalt(II) and Chromium(III)

P. SINGH, (Miss) VINITA RANI, G.C. GUPTA and V. SINGH

Department of Chemistry, S. S. V. College, Hapur

Manuscript received 23 July 1980, accepted 26 May 1984

Ce^{III}, Sm^{III}, Gd^{III}, Dy^{III}, Co^{II} and Cr^{III} complexes of tridentate Shiff base derived from the condensation of *o*-aminophenol and β-naphthylglyoxal have been prepared and studied by

TABLE 1—COLOUR, M.P., STABILITY CONSTANT AND ANALYTICAL DATAS OF THE COMPLEXES

Complex	Colour	M.p. °C	Analysis % ; Found/(Calcd.) C	H	N	Metal	K	ΔF kcal mol^{-1}
$[Ce(C_{18}H_{12}O_2N)_2]Cl$	Light brown	200	59.59 (59.00)	3.58 (3.47)	3.86 (3.80)	19.31 (19.28)	1.285×10^{11}	−15.476
$[Dy(C_{18}H_{12}O_2N)_2]NO_3$	Brown	215	55.98 (55.50)	3.10 (3.00)	5.44 (5.40)	20.98 (20.86)	1.568×10^{11}	−15.622
$[Gd(C_{18}H_{12}O_2N)_2]NO_3$	Dark brown	205	56.32 (56.20)	3.13 (3.07)	5.48 (5.35)	20.47 (20.40)	2.007×10^{12}	−17.169
$[Sm(C_{18}H_{12}O_2N)_2]NO_3$	Dark brown	217	56.84 (56.70)	3.16 (3.06)	5.53 (5.38)	19.73 (19.66)	6.621×10^{10}	−15.095
$[Cr(C_{18}H_{12}O_2N)_2]Cl$	Brown	220	68.03 (67.90)	3.78 (3.59)	4.41 (4.48)	8.19 (8.22)	2.717×10^{11}	−15.958
$[Co(C_{18}H_{12}O_2N)_2]$	Brown	230	71.29 (71.04)	3.96 (3.80)	4.62 (4.85)	9.57 (9.62)	1.783×10^{11}	−15.720

absorption and infrared spectroscopy. The stoichiometry of the complexes is established by spectrophotometric methods and elemental analysis. The bindings of the functional groups of the ligand to metal on complexation have been confirmed by infrared spectral study.

Experimental

The ligand β-naphthylidine-*o*-aninophenol was prepared by refluxing the equimolar quantities of both glyoxal and amine in ethanolic medium in presence of a few drops of acetic acid. The content were refluxed for 2 h and then poured into distilled water and the solid filtered off. Finally it was washed with ethanol.

The complexes were prepared by refluxing the metal salt and ligand solution in dimethylformamide in the ratio 1 : 2 for 2 h, and then kept for 2 or 3 days to concentrate the volume. The crystals of the complexes were recovered and washed.

The composition of the complexes was ascertained by the elemental analysis. The infrared spectra (KBr) were taken on a Perkin-Elmer spectrophotometer. The optical density was measured on Bauch and Lomb Spectronic 20.

The colour and melting point of the complexes are given in Table 1.

Results and Discussion

Vosburgh and Cooper's method was applied to determine the number of complexes formed by the interaction of ligand and metal in the system. Equimolar solutions of metal and ligand of different sets were prepared in the ratio 1 : 1, 1 : 2, 1 : 3 and 1 : 4. In the plot between optical density *vs* wavelength the maxima of curves showed the number of the complexes formed in the system. The wavelength at which the maxima occured was suitable for further study and for each system this method was applied. Molar ratio method was applied to determine the composition of the complexes. The curves were plotted between optical density and volume of variant, and break in the curves shows the stoichiometry of all the complexes.

Stability constant K_s was evaluated by molar ratio method by the formula $K_s = (1-\alpha)/4\alpha^3C^2$, where α is the degree of dissociation and C is the total concentration of the complex in mol dm^{-3}.

Free energy, ΔF of complex formation has been evaluated by the equation, $\Delta F = -2.303$ RT log K_s. Stability constant and free energy of the complexes are given in Table 1.

Ir spectral studies : The point of attachment of the ligand with the metal ion has been confirmed by studying the infrared spectra of the ligand and the isolated chelates.

The strong band appearing at 1700 cm^{-1} (C=O) in the ligand is shifted to lower frequency 1680-1690 cm^{-1} on complexation in all the systems, suggesting the formation of C-O-M bonding. The strong band at 1630 cm^{-1} (CH=N) in the ligand was lowered to 1590-1610 cm^{-1} on complexation indicating the formation of M-N bond. Hence, it is concluded that coordination occurs through CH=N and C=O groups. The peak at 3400 cm^{-1} (OH) in the ligand vanished on complexation. Therefore, it is concluded that the third point of attachment of metal to ligand occurs through the oxygen atom of OH group of the ligand.

References

1. A. N. SUNDAR RAM and C. P. PRABHABHARAN, *Indian J. Chem., Sect. A*, 1976, **14**, 536.
2. OM PRAKASH, R. C. GUPTA and S. P. MUSHRAN, *Indian J. Chem., Sect. A*, 1979, **18**, 534.
3. P. K. SHARMA and P. ACHARYA, *J. Indian Chem. Soc.*, 1979, **56**, 961.
4. G. S. MANKU and A. N. BHAT, *Indian J. Chem., Sect. A*, 1977, **15**, 138.
5. M. MOHAN, *Indian J. Chem., Sect. A*, 1977, **15**, 247.
6. B. SEN and R. DOSTEN, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2707.

Complexes of Cobalt(II) and Nickel(II) with 1,2-Dimethylethane-1,2-dionedihydrazone and Their Infrared and Electronic Spectra

H. C. RAI, R. S. THAKUR and R. U. SHARMA

Department of Chemistry, Bihar University, Muzaffarpur-842 001

Manuscript received 31 October 1981, revised 10 November 1983, accepted 26 May 1984

A number of investigations on metal complexes with vicinal dihydrazones having conjugated azomethine linkage have appeared in recent years[1-4] which contain five-membered chelate rings due to bonding through both the nitrogen atoms of the azomethine linkage, the nitrogen atoms of the amino groups remaining uncoordinated. The present communication describes the preparation, properties and characterisation of complexes of Co^{II} and Ni^{II} with 1,2-dimethylethane-1,2-dionedihydrazone of the type, MLX_2 ($X=Cl^-$, Br^- or I^-) wherein nitrogen atoms of the amino groups have also participated in coordination.

Experimental

1,2-Dimethylethane-1,2-dione was of E. Merck quality and hydrazine hydrate of BDH make. All the compounds were prepared under similar experimental conditions described here.

Dichloro-1,2-dimethylethane-1,2-dionedihydrazone nickel(II), $NiCl_2$: 1,2-Dimethylethane-1,2-dione (1.7 g, 0.02 mol) in alcohol was treated with hydrazine hydrate (2.0 g, 0.04 mol) and the resulting mixture was warmed on a water bath for 10 min. The ligand solution thus obtained was added dropwise to an ethanolic solution of nickel(II) chloride hexahydrate (4.8 g, 0.02 mol) with constant stirring. The resulting mixture was refluxed for ~2 h on a water bath. The blue precipitate obtained was filtered, washed with alcohol, then with ether and finally dried at room temperature.

The compounds were analysed for metal, anion and hydrazine contents by standard procedures[5]. Physical measurements were carried out as reported earlier[6]. Analytical data for Ni, Co, N_2H_4 and anions were found to be in agreement with the formulae, MLX_2 within ± 1%.

Results and Discussion

Infrared spectra of the complexes show marked similarity and are strikingly different from the spectra of the ligand as well as complexes of the type, ML_2X_2[1-3]. A comparison of the spectra with those of the ML_2X_2 complexes suggests that although the general features of the spectra of the two classes are similar, marked differences are observed for NH_2 stretching and deformation vibrations due to differences in the mode of coordination of the NH_2 groups.

In the spectra of the uncoordinated ligand, two bands appear in the region 3400-3200 cm^{-1} (NH_2) with similar intensities which are assigned to the asymmetric and symmetric stretching modes. For ML_2X_2 complexes these two bands appear at slightly lower energies with reduced intensity and the changes are attributed to the coordination of the neighbouring imine nitrogen[1-3]. In sharp contrast to these a group of three bands is observed in the spectra of the present complexes at ~ 3280, ~ 3230 and ~ 3130 cm^{-1} characteristic of the N-H stretching vibration of the coordinated NH_2 group. These are analogous to the NH_2 stretch for the bidentate hydrazine. Several earlier workers have assigned these bands, appearing in the region 3400-3200 cm^{-1} having similar characteristics, to the ν_{N-H} of the coordinated NH_2 group. They occur at 50-100 cm^{-1} lower than the corresponding bands of uncoordinated hydrazine. The weakening of the N-H bonds is consequence of coordination of the nitrogen. The bands at ~ 1620 cm^{-1} are assigned to the NH_2. The other bands in the spectra of the complexes due to $\nu_{C=N}$, ν_{C-CH_3} and δ_{C-CH_3} have features similar to the ML_2X_2 complexes[3].

These results suggest that 1,2-dimethylethane-1,2-dionedihydrazone acts as a tetradentate ligand and the complexes may be postulated to have one of the two structures, Fig. 1(a) and 1(b).

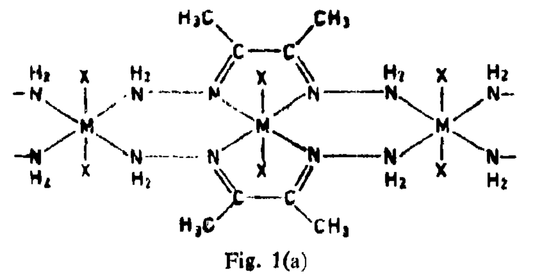


Fig. 1(a)

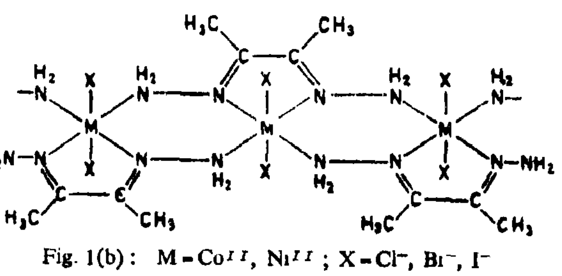


Fig. 1(b): $M = Co^{II}$, Ni^{II} ; $X = Cl^-$, Br^-, I^-

In the structure 1(a), the intermediate bis-complex acts as a coordinating agent through its terminal NH_2 groups on either side forming additional six-membered chelate rings. The remaining two coordination sites required for hexa-coordination being achieved by coordination with the X anions. However, in the latter case each metal ion forms a five-membered chelate ring with the

imine nitrogen atom of the 1,2-dimethylethane-1,2-dionedihydrazone and the terminal NH_2 groups coordinating to the neighbouring metal ions. As the bis-hydrazone complexes could not form any additional complex having the stoichiometry MLX_2, the possibility of the complexes to possess the structure 1(a) is thus eliminated. Further evidence in support of structure 1(b) comes from the electronic spectral data.

The nickel(II) complexes having magnetic moment values in the range 3.00-3.15 B. M. manifest nearly octahedral coordination of ligand atoms about nickel(II) ions with ${}^3A_{2g}$ ground state under octahedral geometry or more precisely ${}^3B_{1g}$ under D_{4h} symmetry.

The spectra of the complexes show two bands in the region 14000-19000 cm^{-1} and a third band at $\sim$24000 cm^{-1}. These resemble the spectral features of NiL_2X_2 complexes implying that all the metal ion centres have similar ligand fields. Similar ligand fields would arise provided the complexes possess a polymeric structure 1(b) wherein each metal ion is coordinated to two imine nitrogen atoms and two NH_2 groups from the two adjacent molecules rather than the structure 1(a) wherein each bis-complex functions as ligands and bonding to metal ions on either side as an exo-bi-bidentate ligand. The structure 1(a) is expected to have two kinds of ligand fields about the metal ions and consequently the split components of the orbitally triplets in an octahedral field will have different energies leading to a larger number of electronic transitions as compared to the structure 1(b). The observed spectral data showing only three bands in the ligand field region lead us to believe that the complexes may have the structure 1(b). The three bands in the electronic spectra of the complexes are attributed to the transitions,

$${}^3A_{2g} \leftarrow {}^3B_{1g},\ {}^3E_g \leftarrow {}^3B_{1g} \text{ and } {}^3T_{1g}(P) \leftarrow {}^3A_{2g}.$$

The cobalt(II) complexes possess magnetic moment values in the range 5.00-5.20 B.M. which correspond to an octahedral stereochemistry about the metal ion having the ground state ${}^4F$ which splits into ${}^4T_{1g}$, ${}^4T_{2g}$ and ${}^4A_{2g}$ whose energy levels increase successively and ${}^4P$ terms transforming as ${}^4T_{1g}$ under D_{4h} symmetry. One of the important features of the electronic spectra of the complexes is the appearance of a strong charge-transfer band above 20000 cm^{-1} and has in a few cases impeded resolution of the spectra in this region.

Though electronic spectra of several cobalt(II) complexes have been reported[6-11], their assignments have not been unambiguous. The ligand field transitions, ${}^4A_{2g} \leftarrow {}^4T_{1g}$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$ appear in the visible region of spectra, the former being always weak, is scarcely observed. On the other hand, the latter appears as a relatively intense band with some amount of structure. The present cobalt(II) complexes exhibit a multiplet band structure in the region 16000-19000 cm^{-1}, the band width spreading over *ca.* 3000 cm^{-1}, which can be assigned to the transition ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$. It may further be pointed out that the spectral features have similarity to the spectra of the bis-complexes, CoL_2X_2 implying similar ligand fields about the cobalt(II) ions providing evidence in favour of the structure 1(b) and ruling out the possibility of structure 1(a).

Acknowledgement

The authors express their indebtedness to Prof. B. Sahoo, Department of Chemistry, I.I.T., Kharagpur, for his interest, encouragement and discussions and also thank Dr. T. Sharma, Head, University Department of Chemistry, Bihar University, Muzaffarpur, for facilities.

References

1. R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, 1956, **78**, 6016.
2. R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, 1960, **82**, 3491.
3. H. C. Rai and B. Sahoo, *J. Indian Chem. Soc.*, 1976, **53**, 646.
4. J. Chakrabarty and B Sahoo, *Indian J. Chem*, *Sect. A*, 1980, **19**, 441.
5. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", Longmans, London, 1961, pp. 380, 460, 480, 568, 569.
6. A. Abragam and M. H. L. Pryce, *Proc. R. Soc. London, Ser. A*, 1951, **206**, 173.
7. S. Koide, *Phil. Mag.*, 1959, **4**, 243.
8. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968, pp. 318-333.
9. F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, 1960, **82**, 2979.
10. J. Chakrabarty and B. Sahoo, *Indian J. Chem.*, *Sect. A*, 1981, **20**, 431.
11. R. S. Thakur, R. U. Sharma and H. C. Rai, *Indian J. Chem.*, *Sect. A*, 1982, **21**, 837.

Infrared Studies of Some Metal Periodates*

H. G. MUKHERJEE, S. B. SARKAR, B. MANDAL
and
B. K. CHAUDHURI

Department of Chemistry, University College of Science, University of Calcutta, Calcutta-700 009

Manuscript received 5 November 1982, revised 21 March 1984, accepted 26 May 1984

PERIODATE ion is a very good oxidising and stabilizing agent. It can stabilize the unusual oxidation states of many transition metal ions. Very often periodates give insoluble compounds making them unsuitable for *X*-ray crystallographic studies. In these cases infrared study is very useful to characterise the bondings. In this attempt we have studied some periodate compounds of

* Paper presented at the Conference on Analytical Chemistry and Applied Spectroscopy, 1980, Pittsburg, U.S.A.

iron(III), cobalt(III) nickel(IV), cerium(IV), uranium(VI) and gallium(III). Only cobalt compound is water soluble and the rest are insoluble. It is only very recently that a periodate compound of cobalt has been studied by *X*-ray crystallographic method[4].

Experimental

Cobalt(III) and iron(III) compounds were prepared following the methods outlined in the literature[1-3]. Chemical analyses confirmed their composition and formulated as $Na_5[Co(H_2IO_6)_2(OH)_2].8H_2O$, $H_3[Co_4I_3O_{24}H_{12}].6H_2O$, $Na_5[Fe(H_2IO_6)_2(OH)_2].6H_2O$, $H_3[Fe_4I_3O_{24}H_{12}]$.

Uranyl compound: To a hot (below 80°) solution of $UO_2(NO_3)_2.6H_2O$(1 g in 25 ml water) a 75 ml solution containing potassium hydroxide (12 g) and KIO_4 (1.4 g) was added with vigorous stirring for 5-10 min. The mixture was then allowed to settle and filtered. To the bright yellow filtrate lithium sulphate solution was added. The resulting light yellow precipitate was filtered, washed with water until the *p*H of the final washing reached 8. It was further washed with absolute ethanol followed by ether, dried over $CaCl_2$ and then analysed. The empirical formula of the compound was found to be $Li_{16}[UO_2I_6O_{30}].8H_2O$.

Cerium compound: Ceric ammonium nitrate (1 g) was dissolved in distilled water (10 ml) previously acidified with conc. HNO_3, and filtered. The *p*H of the solution was adjusted to 1.15-1.50 and then mixed with a solution of $NaIO_4$ (2 g in 30 ml water). A yellow solid obtained was filtered, washed thorougly to free it from cerium and then dissolved in KOH solution (3*N*) by the addition of requisite amount of $NaIO_4$. To the resulting solution a concentrated solution of sodium nitrate was added and a light yellow precipitate obtained was filtered, washed with water followed by methanol until free from alkali, cerium nitrate and periodate. The product was dried over conc. H_2SO_4 and analysed. The empirical formula of the compound was found to be $NaCeIO_6.H_2O$.

Nickel compound: $NiSO_4.7H_2O$ solution (2 g in 10 ml water) was added to KOH solution (50 ml, 4*N*) containing KIO_4 (1 g). Potassium persulphate (5 g) was added to the solution and stirred for ~3 h. A brown solution obtained was filtered. To the filtrate an equivalent amount of lithium sulphate solution was added. The resulting brown precipitate was filtered, washed with water to free it from alkali and other impurities, followed by ether and finally dried in a vacuum desiccator. On analysis the empirical formula of the compound was found to be $Li_2[NiI_6O_{24}].6H_2O$.

Gallium compounds: (i) Gallium sulphate (0.0093 mol) solution was added to KIO_4 (0.02 mol) in KOH solution (3*N*). The mixture was stirred for 4 h with slow heating. The solution obtained was filtered and an equivalent amount of lithium sulphate solution was added to the filtrate. The white precipitate obtained was filtered, washed with alcohol (1 : 1) and finally with water to free it from alkali, lithium periodate and other impurities. The product was further washed with ethanol and air dried. On analysis the empirical formula of the compound was found to be $Li_7[Ga(IO_6)_2].4H_2O$.

(ii) Gallium sulphate (0.0117 mol in 25 ml water) was stirred with an equivalent amount of $NaIO_4$ in water for 2-3 h. *p*H of the solution was 3-4. The white precipitate obtained was filtered, washed with aqueous ethanol (1 : 1), dried and analysed. The compound was found to be $Ga_3(IO_6)_3.H_2O$.

The infrared spectra of the compounds were recorded on Perkin-Elmer 577 spectrophotometer in the CsI phase.

Results and Discussion

The compounds can be divided apparently into three categories : simple salts, simple complexes, and polymerised or condensed complexes. But it has not been possible to classify them under the above categories only from their infrared studies. All these compounds show peaks more or less in the same region, with occasional shifting of the peak positions consistent with change in molecular weight of the compounds as well as environment of the characteristic groups (Table 1).

Strong and broad ir bands have been found at 3600-2600 cm^{-1} (OH). Broadening of the bands suggest hydrogen bonding of the type O-H...O. Deformation vibrations of the water molecules appear at 1650-1575 cm^{-1}. A large number of absorptions are observed at 1380-1035 cm^{-1} as a result of I-OH deformation. Expected peaks due to M-OH deformation in the compounds (2) and (4) seem to overlap with that of I-OH deformation, because M-OH are generally obtained in this range[6]. At the lower range (below 850 cm^{-1}) complicated bands are observed for most of the compounds. Peaks at 770-550 cm^{-1} are attributed to I-O stretching vibrations. Some authors[7] observed a band with various peaks at 590-700 cm^{-1} attributed to δ_{OH}. It is rather difficult to distinguish between ν_{I-O} and δ_{OH}.

Several peaks at 530-215 cm^{-1} are probably due to O-I-O deformations. Metal-oxygen vibrations may also appear in this region[8-10]. It is, however, difficult to distinguish the bands in this region. Probability of the I-O-I bond present in the compound (5) is supported by the peaks 600 and 450 cm^{-1} which can be assigned to I-O-I stretching and bending modes, respectively[8].

Regarding additional peaks, 880 cm^{-1} for compound (7) can be assigned to U=O, and 940 cm^{-1} for (9) is probably due to OH deformation. Additional peak at 850 cm^{-1} in case of (1) can be assigned to Fe-O-Fe bridging. Other peaks are difficult to characterise.

TABLE 1—IR SPECTRA OF COMPOUNDS (cm^{-1})

Sl. no.	Compounds	ν_{OH}	δ_{I-OH}	δ_{H_2O}	δ_{I-OH}	ν_{I-O}	$\tau_{I-O(H)}$	ν_{I-O-I}	δ_{O-I-O}	δ_{I-O-I}	Additional peaks
1.	$H_8[Fe_4I_8O_{44}H_{12}]$	3410-3490s,b	–	1650m	1360w	687m,b	–	–	500vs 420s 300s 230m 220m	–	850m
2.	$Na_8[Fe(H_2IO_6)_2(OH)_2].6H_2O$	3540 3480 3400vs	2250w	1635, 1615m	1380w 1150w 1015sh	615s	–	–	475s 400s 255m 235m 215m	–	–
3.	$H_8[Co_4I_8O_{44}H_{12}].6H_2O$	3350-2600	2230 v,w	1530m	1130w 1080w	780s 670m 575m 550m	–	–	475m 350s 290sh 275sh	–	..
4.	$Na_8[Co(H_2IO_6)_2(OH)_2].8H_2O$	3600-3100s,b	2260w	1610-1595m	1300m 1270w 1165sh 1080w	770s 720w 630w	880w	–	530w,b 390w 340w 320w 300w 255sh	–	–
5.	$Li_8[NiI_6O_{24}].6H_2O$	3500-3360s,b	–	1650m	–	710m,b	–	600w	–	450m,b	–
6.	$NaCeIO_6.H_2O$	3380-3110s,b	2380m	1600-1575w,b	1460w	700-670s,b	–	–	450-420 m,b 370vw 210m,s	–	–
7.	$Li_{14}[UO_2I_6O_{30}].8H_2O$	3400s,b	2200w	1640w,b	1390m	720-650vs,b	–	–	480-400 vs,b 285w 220w	–	880m
8.	$Li_7[Ga(IO_6)_2].4H_2O$	3520-3430m	–	1640w,b	–	700s 620s	–	–	310sh 235w 215w	–	–
9.	$Ga_5(IO_6)_3.H_2O$	3500-3080s,b	2320w	1625-1600m,b	1380s 1170-1035 w,b	720-650m,b	–	–	480s 385m 290s 250m	–	940vw

vs = very strong, s = strong, m = medium, sh = shoulder, b = broad, vw = very weak.

Acknowledgement

The authors acknowledge the help of Professor O. P. Vig, Head of the Department of Chemistry, Punjab University, and Dr. R G. Bhattacharya, Department of Chemistry, Jadavpur University, and C. D. R. I., Lucknow for recording ir spectra. They also thank the U. G. C., New Delhi for a Teacher Fellowship to one of them (B.M.) and financial assistance to another (B.K.C).

References

1. M. J. M. CAMPBELL and C. J. NYMAN, *Inorg. Chem.*, 1962, **1**, 842.
2. C. J. NYMAN and R. A. PLANE, *J Am. Chem Soc.*, 1961, **83**, 2617.
3. "Inorganic Synthesis", ed. S. YOUNG TYRES, Jr., McGraw Hill, New York, 1967, Vol. 9, p. 142.
4. L. C. W. BAKER, L. LEBIODA, J. GROCHOWSKI and H. G. MUKHERJEE, *J. Am. Chem. Soc.*, 1980, **102**, 3274.
5. A. H. J. LOKIO and J. R. KYRKI, *Chem. Abstr.*, 1972, **76**, 30231, 30232.
6. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd. ed., Wiley-Interscience, New York, 1969, p. 82.
7. R. BLINE and D. HAZDI, *Mol. Phys.*, 1958, **1**, 391.
8. B. HAJEK and J. HRADILOVA, *Collect. Czech. Chem. Commun.*, 1971, **36**, 3765.
9. A. H. J. LOKIO and J. R. KYRKI, *Chem. Abstr.*, 1974, **80**, 9904.
10. H. SIEBERT and G. WIEGHARDT, *Spectrochim. Acta, Part A*, 1971, **27**, 1677.

Synthesis and Studies on Some Mixed-Metal Periodates of Cerium(IV)

H. G. MUKHERJEE* and B. K. CHAUDHURI

Department of Chemistry, University College of Science, University of Calcutta, Calcutta-700 009

and

L. C. W. BAKER

Georgetown University, Washington, D. C., U.S.A.

Manuscript received 4 April 1983, revised 21 March 1984, accepted 26 May 1984

MIXED metal periodates of the type $M^IM^{IV}IO_6$ (M^I=Na, K, NH_4, Rb, Cs, and M^{IV}=Ni, Mn, Pb, Ce, Sn) are known[1-4]. Periodate of nickel(IV) was first prepared[1] followed[2] by Ni^{IV} and Mn^{IV}. The compounds of lead, germanium and

tin have been prepared recently[2-4]. Although ceric periodates are known[5-8], preparation of mixed metal ceriperiodates has not been attempted so far. This is for the first time that mixed metal rare-earth periodates have been prepared and their properties studied. The work of Alimarin *et al.*[7] was repeated for the preparation of potassium ceriperiodate, but we were unsuccessful. Some studies on $CeHIO_6.4H_2O$ have also been carried out.

Experimental

Ceric hydrogen periodate: $CeHIO_6.4H_2O$: $NaIO_4$ was added to a solution of ceric ammonium nitrate maintained at *p*H 1.15-1.50. The freshly prepared compound was dissolved in excess KOH (3 *N*) containing $NaIO_4$. To this was added a concentrated solution of sodium nitrate and stirred well. A light yellow precipitate settled, washed with water to free it from alkali, cerium and nitrate ions, kept in a vacuum desiccator for 48 h and stored over conc. H_2SO_4. The composition $NaCeIO_6.H_2O$ was in consistent with the percentages found.

The same compound was also prepared by stirring $CeHIO_6.XH_2O$ vigorously with caustic soda solution (50 ml, 3 *N*) for about 12 h at 35-40°. The yellow product was filtered, washed with methanol and water and finally dried over conc. H_2SO_4.

Lithium ceriperiodate: Ceric ammon nitrate (40 ml, 0.274*M*), KIO_4 (30 ml, 0.29*M*) and KOH (30 ml, 17.85*M*) were mixed in 100 ml KOH (4.46*M*) and with stirring lithium nitrate was added. The light yellow product was washed with aqueous methanol (1 : 1) and dried over conc. H_2SO_4. The formula of the compound was found to be $LiCeIO_6.H_2O$.

Potassium ceriperiodate: Aqueous methanol (1 : 1) was added to the solution of $CeHIO_6.XH_2O$ in KOH (3 *N*) and the resulting precipitated product was washed successively with water, methanol and ether.

Magnetic susceptibility was measured in a Gouy magnetic balance at 29°. Uv spectra were recorded on a Varian Techtron automatic recording spectrophotometer and the visible spectra on a Hilger UNISPEK spectrophotometer. Mull spectra were taken using liquid paraffin as base. Spectra of $CeHIO_6.4H_2O$ was taken in KOH solution (3 *N*). Ir spectra were recorded on Perkin-Elmer and Unicam SP 1000 spectrophotometer. *X*-Ray diffractograms were recorded on a Philips PW 1140 diffractometer using Fe-K_α radiation. Thermal studies were carried out on a Paulik-Paulik-Erdey MOM OD-102 derivetograph using platinum crucible at the heating rate 3° min^{-1}.

Results and Discussion

Uv and visible spectra: The results of the spectral data are reoorded in Table 1.

TABLE 1—ELECTRONIC SPECTRA OF THE COMPOUNDS

Compounds	λ_{max} nm	$\nu \times 10^4$	Intensity*	Assignment**
$NaCeIO_6.H_2O$	430	2.32	m	CT
	207	4.83	vs	CT
$LiCeIO_6.H_2O$	430	2.32	m	CT
	195	5.12	vs	CT
$CeHIO_6.XH_2O$	425	2.35	m	CT
	200	5.00	vs	CT
$CeHIO_6.XH_2O$ in 3*N* KOH	400	2.50	s	CT
	360-290	(2.77-3.44)	h	CT
	220	4.54	vs	CT

*m = medium, vs = very strong, s = strong, h = hump.
**CT = charge transfer.

The peaks around 400 nm are due to metal-ligand charge transfer and those around 200 nm are characteristic of IO_6^{5-} species. The appearance of an absorption maxima at 300 nm was noted for a ceric periodate complex in alkaline medium[9].

Ir spectra: Strong and broad band at 3500-2800 cm^{-1} (stretching OH) is due to hydrogen bonding of the type O-H...O. Deformation vibrations of water molecules occur at higher values for the sodium, potassium and lithium salts. The number of bands are three with the alkali metal salts and only one with the ceric periodate. I-OH vibration occuring at higher wave number for the mixed-metal periodates may be due to strengthening of this bond. The bands at 2350 cm^{-1} may be assigned to 2δ (I-OH) vibration[10]. Similarly, I-O bond seems stronger for the metal periodates. The results are shown in the Table 2.

X-Ray diffractogram: The results show the compounds to be of amorphous variety. Two halos are observed for $CeHIO_6.4H_2O$ and $LiCeIO_6.H_2O$ but only one for $NaCeIO_6.H_2O$. The halo for the sodium salt starts from 30° and extends upto 45° corresponding to d value of 3.74 and 2.53Å, respectively. The peak values correspond to a plane of interplaner spacing 3.01Å. For the lithium salt the first halo starts from 20° (d=5.58Å) and extends upto 31.3° (d=3.59Å), with the peak value d = 4.44Å. The second halo starts from 53° (d=2.17Å) and extends upto 58.5° (d=1.98Å), with the peak value d=2 09Å. For $CeHIO_6.4H_2O$, the first halo extends from 27° (d=4.15Å) to 37° (d=3.05Å), corresponding to a peak value d = 3.54Å. The second halo extends from 38° (d=2.98Å) to 49° (d = 2.34Å) corresponding to the peak value d=2.53Å.

TABLE 2—INFRARED SPECTRA OF COMPOUNDS

$CeHIO_6.4H_2O$	$NaCeIO_6.H_2O$	$LiCeIO_6.H_2O$	$KCeIO_6.XH_2O$	Assignment
3500-2830s, b	3380-3100s, b	3500-3240s, b	3500-3200s, b	ν_{OH}
2370-2320w, b	2380m	2380m	2340m	$2\delta_{IOH}$
1610s	1600-1575w, b	1650m	1650m	δ_{H_2O}
		1560m	1555m	
		1540m	1540m	
1300w	1460w	14-0w	1460w	δ_{IOH}
1160w		1420w	1450w	
		1340b, w	1330w	
		1060b, w		
720s	700-670s, b	780s, b	750-680s, b	δ_{IO}
690-670b		720-680s, b		ν_{IOH}
560m				
420s	450-420m, b			δ_{OIO}
350s				
270sh	370w			
	220m, s			

s = strong, b = broad, w = weak, m = medium.

Thermal study: The results of thermal study are shown below.

(i) $CeHIO_6.4H_2O \xrightarrow{60-270^\circ} CeHIO_6.H_2O + 3H_2O$

$CeHIO_6.H_2O \xrightarrow{275-310^\circ} CeHIO_6 + H_2O$

$2CeHIO_6 \xrightarrow{>620^\circ} 2CeO_2 + H_2O + I_2 + 7/2O_2$

(ii) $LiCeIO_6.H_2O \xrightarrow{70^\circ-145^\circ} LiCeIO_6 + H_2O$

$LiCeIO_6 \xrightarrow{580^\circ} LiI + CeO_2 + 2O_2$

$2LiI + O_2 \xrightarrow{\sim 1000^\circ} Li_2O + I_2 + 3/2O_2$

(iii) $NaCeIO_6.H_2O \xrightarrow{55-280^\circ} NaCeIO_6 + H_2O$

$2NaCeIO_6 \longrightarrow Na_2O + 2CeO_2 + I_2 + 7/2O_2$

The compound $CeHIO_6.4H_2O$ was found to be stable upto 60°. The product obtained at 270° was $CeHIO_6.H_2O$ which was stable upto 310°. The product $CeHIO_6$ was stable at 360-445°. CeO_2 was obtained as residue after 620°. $LiCeIO_6.H_2O$ was found to be stable upto 70°. Loss of water moleoules took place at 70-145°, followed by a gradual loss in weight. The product obtained at 580° was a mixture of LiI and CeO_2. After 1000° it became Li_2O and CeO_2. $NaCeIO_6.H_2O$ was stable upto 55° followed by gradual loss of water upto 280°. The end product obtained after 720° was a mixture of Na_2O and CeO_2.

The compounds are all yellow. The deepening of colour of the compounds follows the order, Li <Na<K. The solubility of the salts in water is of the order K>Na>Li.

The compounds behaved as oxidising agents in dilute sulphuric acid medium and oxidised three moles of Mohr salt per mole of the compound corresponding to the reduction of Ce^{IV} to Ce^{III} and of periodate to iodate, and consumed nine-equivalents of sodium thiosulphate per mole of the compound to titrate the liberated iodine when potassium iodide was added to the H_2SO_4 solution.

$$2CeIO_6^- + 6Fe^{2+} + 12H^+ = 2Ce^{3+} + 2IO_3^- + 6Fe^{3+} + 6H_2O$$

$$2CeIO_6^- + 16I^- + 24H^+ = 2Ce^{3+} + 9I_2 + 12H_2O.$$

Potentiometric titration with Mohr salt could not be carried out with the H_2SO_4 solution of these compounds.

The calculated molar susceptibility values, -68.19×10^{-6} for sodium salt and -47.79×10^{-6} for lithium salt confirmed the compounds to be diamagnetic.

Thermal studies have confirmed that the compounds are of equal stability and are stable at the room temperature. The end product is CeO_2 for ceric periodate and is a mixture of CeO_2 and alkali metal. $CeHIO_6$ is stable over a wide range of temperature.

Infrared spectral studies have confirmed the presence of stretching and bending vibrations of OH, I-OH, H_2O, I-O, IO-(H) and OIO groups. Hydrogen bondings are also present. Appearance of peaks nearly in the same region show similarity in the structures of the mixed-metal periodates. The arrangement of six oxygen atoms round iodine may not be symmetrical as more peaks appear in the δ_{IOH} and, δ_{OIO} vibrations[11]. *X*-Ray study reveals that the compounds are amorphous.

Electronic spectra confirm the presence of IO_6^{5-} in all these compounds[12]. The shift in absorption maxima in this region, may be due to the size effect of the alkali metals in the IO_6^{5-} environment. Appearance of absorption maxima at 430 nm in

all three compounds indicates their structural similarity.

Acknowledgement

The authors acknowledge the help of Dr. N. Roychaudhuri, Department of Chemistry, Indian Association for the Cultivation of Science, Calcutta for the thermal studies, Dr. R. Guha, Mineral Physics Department, Geological Survey of India, Calcutta for recording *X*-ray. One of the authors (B. K. C.) is the recipient of financial assistance from U. G. C., New Delhi.

References

1. P. RAY and B. SARMA, *J. Indian Chem. Soc.*, 1948, **25**, 205.
2. I. REIMER and M. W. LISTER, *Can. J. Chem.*, 1961, **39**, 2431.
3. R. FRYDRYCH, *Chem. Ber.*, 1967, **100**, 3588 ; 1970, **103**, 327 ; 1972, **105**, 2427.
4. M. NATARAJAN, P. RAMAMURTHY and E. A. SECCO, *Can. J. Chem.*, 1974, **52**, 3187.
5. P. C. ROYCHAUDHURI, *J. Indian Chem. Soc.*, 1941, **18**, 335.
6. M. VENKATARAMANIAH and B. S. V. B. RAO, *Curr. Sci.*, 1949, **18**, 248.
7. I. P. ALIMARIN, I. V. PUZDRENKOVA and O. A. SHIRYAEVA, *Vestn. Mosk. Univ. Khim.*, 1962, **17**, 61.
8. A. H. J. LOKIO, *Acta Chem. Scand.*, 1973. **27**, 146.
9. I. P. ALIMARIN and I. V. PUZDRENKOVA, *Vestn. Mosk. Univ. Khim.*, 1959, **14**, 213.
10. B. K. CHAUDHURI and H. G. MUKHERJEE, *J. Indian Chem. Soc.*, 1979, **56**, 1098 ; 1982, **59**, 930.
11. A. H. J. LOKIO, *Finn. Chem. Lett.*, 1974, **1**, 5.
12. C. E. CROUTHAMEL, H. V. MEEK, D. S. MARTIN and C. V. BANKS, *J. Am. Chem. Soc.*, 1949, **71**, 3031 ; 1951, **73**, 82.

Potentiometric Studies of Some Cerium(IV) and Dysprosium(III) Complexes

A. A. PATWARDHAN and A. P. JOSHI*

Department of Chemistry, Nagpur University, Nagpur-440 010

Manuscript received 7 January 1983, revised 4 October 1983, accepted 26 May 1984

THE present work was carried out to study the complexing properties of cerium(IV) and dysprosium(III) with 1-cyclohexyledene-2-benzyledene succinic acid (CHBSA), 1-cyclohexyledene succinic acid (CHSA), and 1-phenyl-3-thiobenzoyl thiocarbamide (PTT) at a fixed ionic strength and temperature. The communication reports for the first time the proton-ligand stability constants of all the three ligands and the metal-ligand stability constants of the complexes of CHBSA and CHSA with both cerium and dysprosium. The method used was the Bjerrum-Calvin titration technique[1,2] as adapted by Irving and Rossotti[3].

Experimental

Reagents : Stock solutions ($2.0\times10^{-2}M$) of both cerium and dysprosium were prepared using ceric ammonium sulphate (AR, SM) and dysprosium chloride (Indian Rare Earths) in calculated quantity of perchloric acid solution to prevent hydrolysis.

All the three ligands, namely CHBSA[4], CHSA[4] and PTT[5,6] were prepared and purified. The stock solutions ($2.0\times10^{-2}M$) of CHBSA and CHSA were prepared in alcohol and PTT in acetone. The solutions of the ligands were prepared by suitable dilution of the stock solutions so that ligands were present in 30% alcoholic or acetone solution. The ligands solutions were standardized potentiometrically.

Sodium hydroxide pellets (EM) were dissolved in CO_2-free distilled water and kept overnight. A portion of it was diluted and its concentration determined by titrating it potentiometrically against standard potassium hydrogen phthalate ($0.1M$).

The stock solution of perchloric acid (EM) ($0.1M$) was prepared and standardized potentiometrically with a standard sodium hydroxide solution.

Potassium chloride (AnalaR) solution ($1.0M$) was used to maintain the ionic strength of the system and was prepared by dissolving a known weight in CO_2-free distilled water.

Apparatus : Elico *p*H meter (sensitivity ±0.05) with glass-calomel electrode system was used for *p*H measurements. The *p*H meter was calibrated by a suitable buffer before use. All experiments were carried out at room temperature (27°).

Bjerrum-Calvin titration :

The three mixtures were prepared as follows: (A) 10 ml $10^{-1}M$ $HClO_4$ + 80 ml double distilled water + 10 ml M KCl solution, (B) 10 ml $10^{-1}M$ $HClO_4$ + 10 ml $2\times10^{-2}M$ ligand solution + 20 ml redistilled acetone/alcohol + 10 ml M KCl solution +50 ml double distilled water, and (C) 10 ml $10^{-1}M$ $HClO_4$ + 10 ml $2\times10^{-2}M$ ligand solution +20 ml redistilled acetone/alcohol+10 ml $2\times10^{-2}M$ metal ion solution + 10 ml M KCl solution+40 ml double distilled water. These solutions were titrated with a standard sodium hydroxide solution. The three curves obtained by plotting *p*H against the volume of alkali added were referred to as (a) acid titration curve, (b) ligand titration curve and (c) complex titration curve.

Results and Discussion

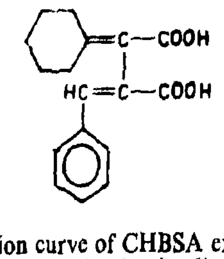
The calculation of *practical* proton ligand stability constant was carried out by plotting a graph of $\bar{n}_A$ *vs* *p*H and applying the method of interpolation at half $\bar{n}_A$ values and interpolation at various $\bar{n}_A$ values. The values with error limit of $\pm$ 0.03 are given in Table 1.

TABLE 1—VALUES OF PROTONATION CONSTANTS OF LIGANDS

Temp. = 27°

Ligands	$\log K_1^H$	$\log K_2^H$	log B
CHBSA	7.46	5.03	12.49
CHSA	5.75	–	5.75
PTT	10.72	–	10.72

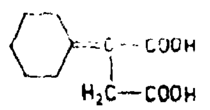
CHBSA has the following structure.



The formation curve of CHBSA extends from 0 to 2 on the $\bar{n}_A$ scale indicating its dissociation as

$$H_2CHBSA \overset{K_1}{\rightleftharpoons} H^+ + HCHBSA^- \overset{K_2}{\rightleftharpoons} H^+ + CHBSA^{2-}.$$

CHSA has the following structure.



The formation curve of CHSA extends between 0 and 1 on the $\bar{n}_A$ scale indicating its dissociation as

$$HCHSA \overset{K_1}{\rightleftharpoons} H^+ + CHSA^-.$$

Although the molecule has two dissociable protons, only one value corresponding to $\log K_1^H$ could be obtained. It may be that the proton present as CH_2COOH dissociates immediately in the solution and its dissociation constant could not be studied in the present work.

PTT, a yet another analytically important reagent[7,8] has the structure $C_6H_5NH\text{-}\overset{\overset{S}{\|}}{C}\text{-}NH\text{-}\overset{\overset{S}{\|}}{C}\text{-}C_6H_5$.

Its formation curve extends between 0 and 1 on the $\bar{n}_A$ scale indicating its dissociation as

$$HPTT \overset{K_1}{\rightleftharpoons} H^+ + PTT^-.$$

With the exception of PTT, in all other cases the complex titration curve (c) extends beyond the ligand titration curve (b). The metal ligand stability constants were calculated by the analysis of the formation curves obtained by plotting $\bar{n}$ against pL. Various computational methods[8] were applied to evaluate the stepwise formation constants. The error limits are $\pm$ 0.03 for $\log K_1$ and $\pm$ 0.05 for $\log K_2$. The mean values of concentration stability constants are given in Table 2.

TABLE 2—VALUES OF CONCENTRATION STABILITY CONSTANTS OF COMPLEXES

Temp. = 27°

Ligand	Ce^{IV} system			Dy^{III} system		
	$\log K_1$	$\log K_2$	log B	$\log K_1$	$\log K_2$	log B
CHBSA	9.08	5.70	14.78	5.56	4.05	9.61
CHSA	–	3.45	–	–	2.85	–

Only one value is obtained in case of CHSA systems. The Ce^{IV}-PTT and Dy^{III}-PTT systems could not be studied as there was a precipitation beyond pH 3.0.

Acknowledgement

Thanks are due to Prof. K. N. Munshi, Head, Department of Chemistry, Nagpur University, for encouragement.

References

1. J. BJERRUM, "Metal Ammine Formation in Aqueous Solution", Hasse, Copenhagen, 1941.
2. M. CALVIN and K. W. WILSON, *J. Am. Chem. Soc.*, 1945, 67, 2003.
3. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904; 1953, 3397.
4. S. BANERJEE, Ph.D. Thesis, Nagpur University, 1980.
5. M. H. DAMLE, Ph.D. Thesis, Nagpur University, 1976.
6. V. W. WALTER and P. M. HELL, *Liebigs Ann. Chem.*, 1969, 22, 727.
7. R. M. UTTARWAR and A. P. JOSHI, *Z. Anal. Chem.*, 1977, 287, 317.
8. S. Q. R. ILYAS and A. P. JOSHI, *Mikrochim. Acta*, 1980, 263.

Anion Exchange Separation of Some Metal Ions in Aqueous-Acetone-Dichloroacetic Acid Media. Part-III

S. V. KULKARNI, S. S. JOSHI and S. K. SOMAN

Department of Chemistry, Shivaji University, Kolhapur-416 004

Manuscript received 17 May 1983, revised 28 November 1983, accepted 26 May 1984

THE use of aqueous-acetone-carboxylic acid media has been shown for ion exchange separation of cations and successful multicomponent separations on anion exchange column were achieved[1,2]. In continuation of our previous work in acetic and chloroacetic acid media, we have now examined the ion-exchange behaviour of Co^{II}, Ni^{II}, Zn^{II}, Mn^{II}, Mg^{II}, Ca^{II}, Cu^{II} and Cd^{II} on anion exchange resin in aqueous solutions of dichloroacetic acid (DCA) with varying concentrations from 0.5 to 3.0*M* at various percentages (0-80%) of acetone. The results, such as distribution coefficients and binary and tertiary mixture separations are reported.

Experimental

All reagents and chemicals were of AR grade (B.D.H., E. Merck). Dowex 21K resin (20-50 mesh, Cl^- form) was obtained from Dow Chemical Co., U.S.A. Standard solutions of Co^{II}, Ni^{II}, Zn^{II}, Mn^{II}, Mg^{II}, Ca^{II}, Cu^{II} and Cd^{II} were prepared by dissolving their chlorides in distilled water and were standardized titrimetrically[3].

The experimental procedure of finding the distribution coefficients and separation of mixtures were as described earlier[1,2]. The resin (1 g) was equilibrated with the solution of metal ion (50 ml, 0.05*M*) in aqueous and differed aqueous acetone-DCA media for 24 h. The weight distribution coefficients[5], K_D were calculated.

Separation of mixtures was carried out by feeding the metal ion mixture (10 ml) on the column of height 20 cm and inner diameter 1 cm. The metal ions were eluted by suitable eluting agents. The effluents were collected in a number of fractions of 10 ml each and were estimated complexometrically[3].

Results and Discussion

The distribution coefficients of the metal ions were found at 0, 20, 40, 60, 80 percentages of acetone and at 0.5, 1, 2, 3 *M* concentrations of DCA. The distribution coefficients of Ni^{II}, Mn^{II}, Mg^{II} at 0.5 and 3 *M* DCA solutions at all percentages of acetone are low, indicating the tendency of these metals to form less stable anionic complexes or not to form such complexes. Cu^{II} and Ca^{II} show the slight tendency to form anionic complexes at 3 *M* DCA. K_D value ($\simeq$50) shows approximately equal distribution of metal ion in solution and resin phases. The distribution coefficients of Zn^{II}, Cd^{II}, Co^{II} and Ca^{II} at 3 *M* DCA are greater than those at 0.5 *M* DCA at the respective acetone percentages. Cu^{II} shows slight rise in K_D at 80% acetone-3 *M* DCA indicating increasing tendency of complex formation at higher percentage of acetone and acid as well. In anion exchange studies it is assumed that a single anionic complex is sorbed on the resin along with excess ligand[4]. The K_D values of Zn^{II}, Co^{II}, Cd^{II} increase with the rise in acetone concentrations which influenced the dielectric constant of media[5]. Acetone does not display the complexing ability in the systems. There is no measurable change in K_D values of Co^{II} in 0.5 *M* DCA at all percentages of acetone. In the case of 3 *M* DCA the distribution coefficients of Co^{II} is $\simeq$ 80 in zero and 20% acetone. These K_D values increase with the rise in acetone percentage. Co^{II} forms a blue coloured anionic complex at 80% acetone-3 *M* DCA, the same stable complex was also observed in 80% acetone-3 *M* acetic acid[1] and chloroacetic acid[2]. Zn^{II} and Cd^{II} show maximum K_D values under the same conditions. The K_D data of the metal ions suggest the following selectivity sequence.

$$Cd > Zn > Co > Ca > Cu > Mn \simeq Mg \simeq Ni.$$

Separations of Co^{II}, Cd^{II} and Zn^{II} from Mg^{II}, Mn^{II}, Cu^{II} and Ca^{II} were carried out by selective sorption technique. On passing the binary mixture, the anionic complexes of Co^{II}, Cd^{II} and Zn^{II} were retained on the column and all other cationic metal ions passed unadsorbed. Co^{II} was eluted with water, Cd^{II} with 5% acetone-0.1 *M* DCA and Zn^{II} with 20% acetone-0.5 *M* DCA. The elution of Co^{II} was easy. Zn^{II} and Cd^{II} were taken up very strongly in comparision to Co^{II}. Therefore, in tertiary mixtures Zn^{II} or Cd^{II} and Co^{II} were retained on column in 80% acetone-3 *M* DCA, while Cu^{II}, Ni^{II}, Mn^{II}, Mg^{II} and Ca^{II} were eluted. Co^{II} was then eluted with 60% acetone-3 *M* DCA, finally Zn^{II} and Cd^{II} were eluted with the above mentioned eluents. The elution of the metal ions started quickly (BTV$\simeq$5-10 ml). It was maximum with $\simeq$40-50 ml eluent (VEP$\simeq$40-50). The separation of each constituent metal ion was carried out with 60 to 90 ml of the eluent (TEV$\simeq$60-90) and took 1-1.5 h.

Quantitative separation of synthetic binary and tertiary mixtures were successfully carried out in the present studies. Mg, Cu, Mn, Ca, Ni metal ions were separated from Co, Cd and Zn. The recovery of each constituent metal ion is more than 90%. The elution curves of the separations of the mixtures are distinct and bell shaped. The metal ions do not interfere with each other and are separated one after the other.

By comparing our present results in DCA with those in acetic acid and CA reported earlier[1,2], it is found that the distribution coefficients of Co^{II}, Cd^{II} and Zn^{II} in 60-80% acetone-3 *M* DCA are greater than those in 60-80% acetone-3 *M* acetic acid or CA. These metal ions are thus strongly held by resin and greater separation factor suggests more accurate separation of ions.

References

1. S. V. Kulkarni, S. K. Soman and S. S. Joshi, *J. Indian Chem. Soc.*, 1983, 60, 779.
2. S. V. Kulkarni, S. K. Soman and S. S. Joshi, *J. Indian Chem. Soc.*, submitted for publication.
3. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", Longmans, London, 1961.
4. M. Qureshi, H. S. Rathore and R. C. Kaushik, *Anal. Chem.*, 1975, 47, 1710.
5. R. P. Bhatnagar and N. C. Jain, *J. Indian Chem. Soc.*, 1980, 57, 168.

Study of Solid State Reaction Between Mercuric Chloride and Sodium Tungstate

INDU BHUSHAN SHARMA* and SULEKHA BATRA

Department of Chemistry, University of Jammu, Jammu-180 001

Manuscript received 2 November 1983, revised 10 April 1984, accepted 17 June 1984

IN the reactivity of solids, exchange reactions are of immense interest. However, because of their complicated nature limited number of such reactions have been studied and their mechanism is also not well understood. In the reaction between MgO and $ZnWO_4$, Jander[1] interpreted the reaction as due to solid state diffusion while Rastogi and Dubey[2] suggested the possibility of vapour phase diffusion in the reaction between mercuric chloride and iodine. The kinetics of such reactions are governed by different mechanisms, depending upon whether the rate determining step is the phase boundary reaction, diffusion process or nucleation [3-5]. In order to examine kinetics and elucidate the mechanism of such reactions, the solid state reaction between $HgCl_2$ and $Na_2WO_4.2H_2O$ has been studied.

Experimental

AnalaR $HgCl_2$ and $Na_2WO_4.2H_2O$ were separately powdered and sieved through mesh.

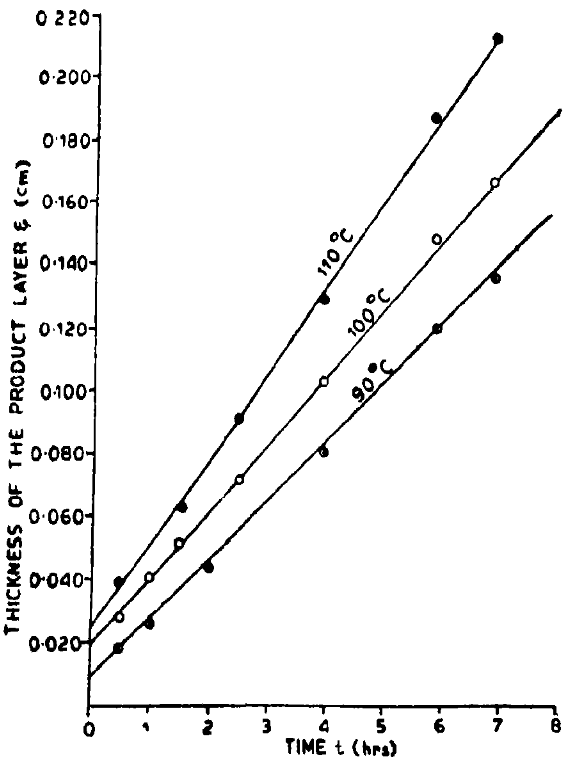


Fig. 1. Plots of ξ versus t in reaction between $HgCl_2$ and $Na_2WO_4.2H_2O$ for reactant particles of size blow 74 microns at different temperatures.

Reaction between $HgCl_2$ and $Na_2WO_4.2H_2O$: Mercuric chloride and sodium tungstate particles of known size were filled in glass tubes (0.8 dia.x10 cm), the former from one end and the latter from the other end, so that the reactants have sharp contact at the centre of the tube. The tubes were sealed at one end and were subjected to a constant pressure (4 kg cm^{-2}) at the other end. The tubes were then placed in a thermostat ($\pm$0.1°). A yellow coloured product layer appeared at the point of contact and was marked to ascertain the direction of diffusion. It was observed that only mercuric chloride diffused through the product layer to react with the other reactant at the product/sodium tungstate interface. The length of the product layer was measured with a travelling microscope (least count $\pm$ 0.002 cm) after certain intervals of time. The experiment was repeated for different temperatures. The data are plotted in Fig. 1.

Role of vapour phase diffusion : The reactants were filled in a glass tube to leave some air gap between the two reactants. The tube was kept in a thermostat (100°) and after 3 h it was observed that the reaction occured on the side of sodium tungstate only. This suggested the occurance of vapour phase diffusion of mercuric chloride which caused the reaction on the side of sodium tungstate. However, the contribution of the vapour phase diffusion is not substantial.

X-Ray diffraction : Mercuric chloride and sodium tungstate were mixed in equimolar ratio by grinding in cyclohexane and heated for 12 h at 100° with intermediate grindings. The *X*-ray diffractogram of the sample gives the following d values (Å) with the relative intensities given in parenthesis. 8.34 (14), 6.66 (5), 5.27 (75), 4.69 (8), 4.55 (4), 4.48 (5), 4.35 (51), 4.09 (16), 3.75 (7), 3.58 (5), 3.44 (7), 3.38 (17), 3.22 (96), 3.07 (4), 3.03 (5), 2.99 (20), 2.90 (5), 2.75 (100), 2.71 (13), 2.41 (11), 2.13 (7), 2.09 (13), 2.06 (9), 1.99 (8), 1.94 (7), 1.90 (5), 1.86(35), 1.75 (27), 1.62 (23), 1.54 (13), 1.44 (13), 1.40 (7), 1.28 (6), 1.22 (10) and 1.18 (12).

The sample prepared for *X*-ray diffraction studies, was washed with distilled water and then dried under vaccum and analysed for Hg by the usual method. The results suggest the formula of the product as $HgWO_4$.

Results and Discussion

The kinetic data of the reaction, as evident from the Fig. 1, follows the linear equation

$$\xi = kt + C,$$

where ξ is the thickness of the product column at any time t, k is the specific reaction rate constant and C is another constant. The k values, calculated from the Fig. 1, are 18.70×10^{-3}, 21.43×10^{-3} and 27.28×10^{-3}cm h^{-1} at 90, 100 and 110°, respectively and the corresponding C values are 8.50×10^{-3}, 20.00×10^{-3} and 25.00×10^{-3}cm. The energy

of activation as calculated from the Arrhenius plot, is 6.5 kcal mol^{-1}.

The *X*-ray diffraction data of the product when compared with the known data for NaCl, suggest the presence of NaCl in addition to some other compounds. The experimental d values 3.22 (95), 2.75 (100), 1.99(10), 1.75 (27), 1.62 (23), 1.40(7), 1.28 (6), 1.22 (10) and 1.18Å (12) correspond to the NaCl structure. Formation of NaCl suggests the stoichiometry of the reaction to be

$$HgCl_2+Na_2WO_4.2H_2O \rightarrow HgWO_4+2NaCl+2H_2O.$$

However, the *X*-ray diffraction data for $HgWO_4$ could not be traced either from the powder diffraction file or from the literature.

The applicability of the linear equation shows that the reaction kinetics are controlled by the phase boundary reaction and the diffusion occurs unhindered[4-6]. The product layer is porous and does not offer any resistance to the diffusion. The low value of the energy of activation 6.5 kcal mol^{-1} substantiates it to be a phase boundary controlled reaction. Substantial increase in C values with rise in temperature suggests vigorous initial reaction at the interface.

Acknowledgement

Thanks are due to Professor P. S. Bassi, Department of Chemistry, Guru Nanak Dev University, for valuable discussions.

References

1. W. JANDER, *Z. Anorg. Chem.*, 1930, 190, 397.
2. R. P. RASTOGI and B. L. DUBEY, *J. Am. Chem. Soc.*, 1967, 89, 200.
3. S. R. YOGANARASIMHAN, "Modern Aspects of Solid State Chemistry", ed. C. N. R. RAO, Plenum Press, New York, 1970, p. 465.
4. A. Z. E. WELCH, "Chemistry of the Solid State", ed. W. E. GARNER, Butterworths, London, 1955, p. 297.
5. H. SCHMALZRIED, "Solid State Reactions", Academic Press, New York. 1974, p. 103.
6. K. HARDEL, *Angew. Chem. Int. Ed Engl.*, 1972, 11, 173.

Effect of Particle Size on the Kinetics of Thermal Dehydration of Silicic Acid Hydrogel

N. K. MITRA, S. SINHAMAHAPATRA and A. BASUMAJUMDAR

Department of Chemical Technology, University of Calcutta, Calcutta-700 009

Manuscript received 17 February 1984, accepted 3 May 1984

IT is generally agreed[1] that the gelation of silica hydrogel is a function of the silica units. Silicic acid hydrogel, normally prepared by destabilisation of an aqueous solution of sodium silicate, has been used as a dehydrating agent in various processes. The phenomena of crystallisation of silicic acid hydrogel which is analogous to the natural ageing of gels to hyalite, opal, chert, chalcedony, *etc.*, has been studied[2] extensively by *X*-ray diffraction with refined DTA and dilatometric method. The surface properties of the silicic acid hydrogel are independent of the state of crystallinity[3]. It was observed[4] that the first small losses of bound water occur at 150° followed by a continuous dehydroxylation above 380°.

The kinetic approach to the study of thermal decomposition of many hydrated materials depends on the rates of reaction and in addition gives basic information about the materials, their structure, surfaces and so forth. It was found[5] that the rate constant during zeolitic dehydration followed an inverse relationship with the total water content of the samples and was explained in terms of position of water molecules in the lattice. It was also shown that the loosely bound channel water also influences strongly but is much less than that of coordinated water. The dehydration kinetics study on alumino-silicate hydrogel[6], taking four different fractions concluded that the reaction followed formal first order kinetics. The activation energies showed little variation with respect to particle size and the absence of any particle size effect on the rate of dehydration was attributed to the highly porous structure of the gel. The deviation from the ideal behaviour at the later stage of dehydration was interpreted on the basis of structure.

In the present investigation an attempt has been made to correlate activation energies of different particle sizes of silicic acid hydrogel.

Experimental

Silicic acid hydrogel was synthesised by cation exchange technique. After proper ageing, they were processed in accordance with reported method[7] to remove the extraneous impurities. The particle size fractions (−20+50), (−50+80), (−80+115), (−115+150), (−150+200) and (−200+300) mesh were prepared with utmost precaution. The materials were again washed, dried and stored at 32±1°. The kinetics of the dehydration process was studied by TG method[6].

Results and Discussion

The isothermal dehydration curves (Figures not shown) showed expotential behaviour and as such first order kinetics was suggested. The initial water concentration (L_α) which can be dehydrated at the experimental temperature and also the rate constant k_1 for the initial stage of dehydration was calculated[6] using equation (1)

$$\text{Log}\Delta L=\frac{-k_1 t}{2.303}+\log L_\alpha\ [1-\exp(-k_1\,\Delta t)]. \quad (1)$$

Where ΔL is the difference between the mass loss at time $(t+\Delta t)$ and t, time interval Δt

TABLE 1 – VALUES OF RATE CONSTANT (k_1) AS DETERMINED FROM LOG ΔL *vs* TIME PLOTS

Hydrogel	Size fraction	k_1 min^{-1} at °C			
		100	130	160	190
Silicic acid	–20+50	0.0794	0.1912	0.2818	0.4215
	–50+80	0.0782	0.1910	0.2814	0.4216
	–80+115	0.0780	0.1908	0.2810	0.4210
	–115+150	0.0778	0.1916	0.2808	0.4212
	–150+200	0.0784	0.1910	0.2815	0.4208
	–200+300	0.0798	0.1918	0.2820	0.4204

TABLE 2 – VALUES OF L_∞ AS DETERMINED FROM GUGGENHEIM EQUATION

Initial wt. of sample = 0.5 (g).

Hydrogel	Size fraction	Mean L_∞(g) at °C			
		100	130	160	190
Silicic acid hydrogel	–20+50				
	–50+80				
	–80+115	0.1150	0.1238	0.1248	0.1250
	–115+150				
	–150+200				
	–200+300				

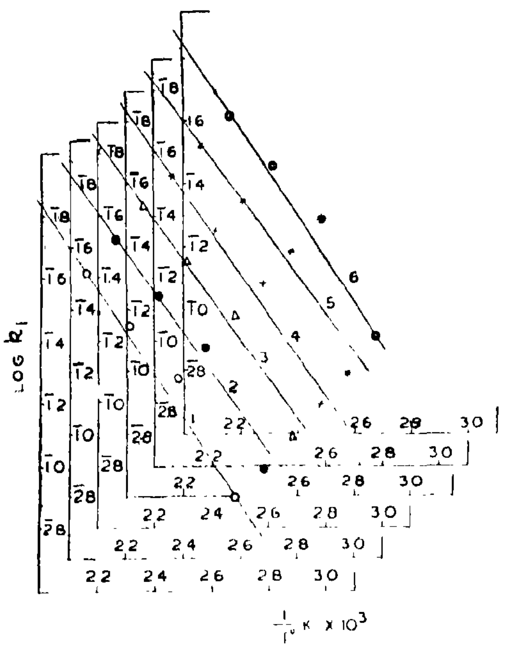


Fig. 1. Arrhenius plots for silicic acid hydrogel of different size fractions for the initial stage of dehydration.

1. O— –20+50 mesh
2. ●— –50+80 ,,
3. △— –80+115 ,,
4. ×— –115+150 ,,
5. •— –150+200 ,,
6. ⊙— –200+300 ,,

between two sets of readings being kept fixed at a value greater than twice the time for 50% dehydration. Using equation (1), the rate constant was calculated from the slope of linear plot of logΔL *vs* t. Knowing Δt and having obtained k_1 from the slope, L_∞ was determined from the intercept on the log axis (Figures not shown). The Guggenheim plots and the values of k_1 and L_∞ are recorded in Table 1 and 2. The activation energy was calculated from the usual Arrhenius plots using the rate constants (Fig. 1).

Gel water is normally characterised by loose bonding with which it is attached to the frame work. Most of the non-crystalline hydrogels contain colloidal water which may be regarded as the extreme case of broken bond water in which the particle size of the solid to which the water is linked is extremely small.

The L_∞ values as determined for the size fraction were found to be nearly the same at a given temperature as expected theoretically, since any deviation in particle size will not alter the final loss at infinite time but might alter the rate of dehydration. Again both k_1 and L_∞ were found to be direct function of temperature which means that the reaction rate and the amount of water expelled from the gel increased with the increase in temperature of heat treatment.

The rate constant values are equal for the different particle sizes at all the temperatures. No positive effect of particle size was observed on the kinetics of dehydration.

From the nature of log [$(L_\infty - L)/L_\infty$] *vs* time curves (not shown for brevity), it was clearly evident that the whole course of reaction did not follow the first order kinetics. As such the limits of applicability of the first order law have been determined from the extent of linearity of these plots. The validity of first order law was found to be influenced slightly by the particle size of the experimental samples, *i.e.* with the decrease in particle size the extent of linearity increased only to a small extent. It varied between 65 to 81.4% (Table 3). This might

TABLE 3 – EXTENT OF VALIDITY OF FIRST ORDER LAW AS DETERMINED FROM LOG [$(L_\infty - L)/L_\infty$] *vs* TIME PLOTS

Hydrogel	Size fraction	First order law as valid upto % dehydration at °C			
		100	130	160	190
Silicic acid hydrogel	–20+50	65.33	71.82	74.88	75.56
	–50+80	66.12	73.08	75.45	77.62
	–80+115	66.38	73.08	76.01	78.12
	–115+150	69.09	74.88	77.09	78.12
	–150+200	70.49	76.01	78.12	80.94
	–200+300	71.81	76.50	78.12	81.37

be due to the fact that with decrease in particle size, the water molecules remaining at the later stages of dehydration, were not influenced to a great extent by the decomposed material and as such extent of linearity increased. It appears that the particle size has practically no influence on the dehydration rates and as such final stage of dehydration was not undertaken in this case.

The calculated values of activation energy from Arrhenius plot (Fig. 1) are presented in Table 4.

TABLE 4 – VALUES OF ACTIVATION ENERGIES FOR INITIAL STAGE OF DEHYDRATION

Hydrogel	Size fraction	Activation energy kcal mol^{-1}
Silicic acid	−20+50	5.95
	−50+80	6.18
	−80+115	5.95
	−115+150	6.17
	−150+200	5.72
	−200+300	6.17

The activation energy values clearly demonstrate the absence of any effect of particle size. Thus no positive effect of particle size was observed on the kinetics of dehydration.

The results of the present study show that (i) particle size has practically no influence on the dehydration rates, (ii) with decrease in particle size, the extent of linearity increased only to a small extent and (iii) no positive effect of particle size was observed on the kinetics of dehydration.

References

1. KIRK-OTHMER, Encyclopedia of Chemical Technology, Interscience, New York, 1969, Vol. 18.
2. O. W. FLORKE, *News Jahrb, Mineral, Monatsch*, 1955, **217**.
3. T. S. TAKAMURA, *Kolloid Z.*, 1958, **157**, 11.
4. J. H. DE BOER, M. E. A. HARMANS and J. M. VLEESKENS, *Koninke Ned. Akad. Westenschap. Proc.*, 1957, **60B**, 45, 54, 233 ; 1958, **61B**, 2, 88.
5. N. K. MITRA, S. GHATAK and S. MITRA, *Indian J. Chem., Sect. A*, 1980, **19**, 195.
6. N. K. MITRA, K. L. ROY and S. MITRA, *Trans. Brit. Ceram. Soc.*, 1975, **74**, 263.
7. N. K. MITRA, S. C. DE, A. CHATTERJEE and S. SINHA-MAHAPATRA, *Indian Ceram.*, 1981, **23**, 235.

Effect of Addition of D(+) Glucose on the B-Z Oscillating Reaction

A. K. DUTT and R. S. BANERJEE*

Department of Chemistry, University College of Science, 92, A. P. C. Road, Calcutta-700 009

Manuscript received 30 December 1982, revised 16 September 1983, accepted 17 June 1984

BELOUSOV-Zhabotinsky[1,2] oscillating reaction has been well studied[3-6] for the last few years. In this communication, the effect of addition of D(+)-glucose, a typical reducing agent, on this reaction has been studied in the presence and absence of it. Gallic acid[7-9] and citric acid[3] have been used as organic substrates and in both the systems, the changes in induction period, time period *etc.* on addition of glucose have been studied in details. Attempts have been made to explain the experimental results in terms of Field, Körös and Noyes (FKN) mechanism[10].

Experimental

In the reaction with citric acid, solid glucose was taken in the reaction vessel. Separate solutions of ceric ammonium sulphate, potassium bromate and citric acid were prepared in sulphuric acid. Ferroin was used as an indicator and the reaction was triggered by the addition of citric acid solution. In case of gallic acid system, solid gallic acid was taken in the reaction vessel and solutions of sulphuric acid, glucose and potassium bromate were added. Here also ferroin was used as an indicator. Use of Ce^{IV} ions was however, unnecessary in this case and the reaction was triggered by the addition of bromate solution.

All solutions were so prepared and mixed that the concentrations in Tables 1 and 2 refer to the concentrations in media. In both cases the reaction mixture was stirred at a fixed rate. The sharp colour changes, blue to green in the case of citric acid, and red to light green in the case of gallic acid were utilised for recording induction period (appearance of first green colour), time period of oscillation, total number of oscillations and total time of oscillation. The experimental results have been summarised in Tables 1 and 2.

TABLE 1 – EFFECT OF D(+) – GLUCOSE ON B-Z SYSTEM CONTAINING GALLIC ACID AT 32°

$[KBrO_3] = 0.1008$ *M*, $[H_2SO_4] = 1.1062$ *M*, [gallic acid] = 0.0399 *M*, [ferroin] ≈ 0.0003 *M*

[D(+)-glucose] *M*	Induction period sec	Average of 3rd and 4th oscillation periods sec	Total no. of oscillations	Total time of oscillations sec
0.0948	94	7	4	25
0.0758	99	5	6	37
0.0472	123	6.5	9	78
0.0190	155	11	19	371
0.0095	146	17	44	1247
nil	156	20	82	2799

TABLE 2 – EFFECT OF D(+)-GLUCOSE ON B-Z SYSTEM CONTAINING CITRIC ACID AT 29°

$[KBrO_3] = 0.0153$ *M*, $[H_2SO_4] = 1.54$ *M*, [citric acid] = 0.457 *M*, [ferroin] = 0.0007 *M*, $[Ce^{4+}] = 0.0037$ *M*

[D(+)-glucose] *M*	Induction period sec	Average of 3rd and 4th oscillation periods sec
0.0580	46	34.5
0.0390	62	42
0.0166	66	58
nil	71	93

Results and Discussion

The experimental results reveal that with both citric and gallic acid the induction period and the oscillation period decrease with increasing concentrations of glucose. For oscillation period, the average of 3rd and 4th oscillation periods has been considered as the first one or two oscillations are anomalous in many systems. In the case of gallic

acid, total number of oscillations and total time of oscillation have also been recorded and these were also found to decrease as the concentration of glucose was increased. Again as no reactant was added during the progress of the reaction, the reaction systems were closed in the thermodynamic sense and the general increase in time period with time in gallic acid system is in conformity with expectations. In case of citric acid, although the first oscillation periods at some glucose concentrations are rather abnormal, the periods in general do not change with time as in the case of sustained oscillations.

The effect of glucose on B-Z reaction can be explained in the light of the FKN mechanism, which involves 3 intermediates, the control intermediate, *i.e.* Br^-, the switched intermediate, *i.e.* bromous acid, and the regeneration intermediate, *i.e.* Fe^{III}, Ce^{IV} ions *etc.* The following are the probable[11] reactions in gallic acid system.

Process A: Reaction of bromide with bromate ion to yield bromine. This last species undergoes fast reaction with gallic acid to generate bromogallic acid (BrHG).

$$BrO_3^- + Br^- + 2H^+ \rightleftharpoons HOBr + HBrO_2 \qquad (A1)$$
$$HBrO_2 + Br^- + H^+ \rightleftharpoons 2HOBr \qquad (A2)$$
$$3 \times HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \qquad (A3)$$
$$3 \times Br_2 + H_2G \longrightarrow Br^- + H^+ + BrHG \qquad (A4)$$
$$BrO_3^- + 2Br^- + 3H_2G + 3H^+ \rightarrow 3BrHG + 3H_2O$$

Process B: Autocatalytic formation of bromous acid with a rapid oxidation of Fe^{2+} to Fe^{3+}.

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2\,BrO_2 + H_2O \qquad (B1a)$$
$$2 \times BrO_2 + Fe^{2+} + H^+ \rightleftharpoons Fe^{3+} + HBrO_2 \qquad (B1b)$$
$$2Fe^{2+} + HBrO_2 + BrO_3^- + 3H^+ \rightarrow 2\,Fe^{3+} + 2HBrO_2 + H_2O \qquad (B1)$$
$$2HBrO_2 \rightleftharpoons HOBr + BrO_3^- + H^+ \qquad (B2)$$

This process is important only when Br^- is under a critical value, bromide ion being an inhibitor of process B by step A2. There is an autocatalytic production of $HBrO_2$ limited by its dismutation in step B2. In the process B, there is a very rapid accumulation of Fe^{3+}.

Process C: A recovery process.

$$n\,Fe^{3+} + BrHG \rightarrow n\,Fe^{2+} + Br^- + \text{oxidized products}$$

This process is the Fe^{3+} oxidation of organic brominated species and generates a bromide ion, thus switching back the reaction to the process A.

As the process A proceeds, the process C continues to deplete Fe^{3+} from the reaction mixture, enabling the bromide concentration to undergo the critical value below which the process B can be switched again.

The reducing property of glucose is perhaps responsible for the decrease of induction period as well as oscillation period. It competes with gallic acid for bromine[12] (or other bromine species in higher oxidation states) as a result of which Br_2 is quickly consumed and process A takes place quickly. It also controls the formation of Br^- because bromogallic acid, which is the chief regenerator of Br^- through process C is formed in smaller amount in its presence. As a result, process B (which is significant at low Br^- concentration) starts sooner. The net result is that the induction period is decreased, oscillation starts sooner and the oscillations are quickly completed decreasing the oscillation period. The total number of oscillations as also the total time of oscillation decrease as bromate is consumed more in each cycle in presence of glucose. As the concentration of glucose is increased, all of these values decrease. It is likely that in citric acid system a similar mechanism is operative.

Acknowledgement

Sincere thanks are due to Dr. N. Dutt of Vidyasagar College, Calcutta for helpful discussion.

References

1. B. P. Belousov, "1958 Collection of Abstracts on Radiation Medicine", Medgiz, Moscow, 1959, p. 145.
2. A. M. Zhabotinskii, *Biofizika*, 1964, **9**, 306.
3. A. Pacault, P. De Kepper, P. Hanusse and A. Rossi, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1975, **281**, 215.
4. P. De Kepper, A. Pacault and A. Rossi, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1976, **282**, 199.
5. P. De Kepper, A. Rossi and A. Pacault, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1976, **283**, 371.
6. J. Boissonade and P. De Kepper, *J. Phys. Chem.*, 1980, **84**, 501.
7. J. S. Babu and K. Srinivasulu, *Z. Phys. Chem.* (*Leipzig*), 1978, **259**, 1191.
8. E. Körös and M. Orban, *Nature* (*London*), 1978, **273**, 371.
9. A. K. Dutt and R. S. Banerjee, *Z. Phys. Chem.* (*Leipzig*), submitted for publication.
10. R. J. Field, E. Körös and R. M. Noyes, *J. Am. Chem. Soc.*, 1972, **94**, 8649.
11. A. Pacault, P. Hanusse, P. De Kepper, C. Vidal and J. Boissonade, *Acc. Chem. Res.*, 1976, **9**, 438.
12. C. Vidal, J. C. Roux and A. Rossi, *J. Am. Chem. Soc.*, 1980, **102**, 1241.

Synthesis and Fungicidal Activity of Some Mixed 5-Pyrazolone and 5-Thiopyrazolone Derivatives

S. DEVI, A. NAYAK** and A. S. MITTRA*

Mayurbhanj Chemical Laboratory, Ravenshaw College, Cuttack-753 003

Manuscript received 19 July 1982, revised 16 April 1984, accepted 17 June 1984

It has been observed from our earlier work on heterocyclic fungicides[1-5] that 5-pyrazonones possess significant fungicidal activity against the rice blast pathogen *Pyricularia oryzae* and the brown leaf spot pathogen *Helminthosporium oryzae*. The survey of literature further reveals that thiopyrazo-

**Regional Research Laboratory, Bhubaneswar-751 013.

lones also exhibit encouraging antifungal activity[6,7]. In view of the marked biological importance associated with these two classes of compounds the present investigation has extended to synthesise some new derivatives containing both the two active nuclei.

Two methods have been adopted for synthesis of 1-aryl-1-(1-phenyl-3-methyl-2-pyrazolin-5-one)-1-(1′-phenyl-3′-methyl-2′-pyrazolin-5-thione) methane. The first method was the Michael addition of 1-phenyl-3-methyl-4-monoarylidene-5-one with 1-phenyl-3-methyl-2-pyrazolin-5-thione. The second method was the Michael addition of the 4-monoarylidene-2-pyrazolin-5-thione with 1-phenyl-3-methyl-2-pyrazolin-5-one. The identity of the compounds prepared by these two different methods were established from their undepressed m.p. and superimposition of ir spectra. The structure of these compounds were established from their elemental analysis, ir and mass spectral studies. The ir spectra of compound I showed bands at ~ 3030 (enolic), 1610 (C=O) and 1130 cm^{-1} (C=S). Further, the mass spectra of this compound record molecular ion (m/e) value 452. The values of 263 and 190 are due to the two parent moieties formed by the rupture of CH-CH linkage. Due to the removal of R-ĊH an absorption appears at 173. Further, the values of 91, 77, 52, 32 and 28 are attributable to $Ph\text{-}\overset{+}{N}$, $\overset{.+}{Ph}$, $\overset{.+}{C_4H_4}$, $\overset{.+}{S}$ and $\overset{.+}{CO}$, respectively which are obtained by similar fragmentation of both the pyrazolone moiety.

The cyclopropane derivatives of these compounds were prepared by dissolving the parent compound I in 20% NaOH solution and subsequent treatment with a saturated solution of iodine-potassium iodide. The structure of these cyclopropane derivatives were confirmed from their elemental analysis and spectral studies. The spectra of II(1) showed bands at 1710 (C=O), 1140 (C=S) and 3200-3110 cm^{-1} (CH in cyclopropane ring), and m/e value of 450 in agreement with its molecular weight.

All the compounds thus prepared were screened for their fungicidal activity against the rice blast pathogen *P. oryzae* and brown leaf spot pathogen *H. oryzae* using the spore germination tests at various concentrations by the standard method. The fungicidal activity of the mixed derivatives at 1000 ppm concentration are recorded in Table 1 and those of their cyclopropane derivatives in Table 2. In general, the rate of germination inhibition was found to be higher in case of the compounds contained in Table 1 than their cyclopropane derivatives. The compounds no. 2, 4, 5, 12 and 15 (Table 1) showed encouraging fungitoxicity against both the pathogens. Further, compounds no. 1, 2, 5, 10 and 17 were active against *P. oryzae*, and 1, 9 and 11 against *H. oryzae*. The compound no. 2 of this series showed highest antifungal activity inhibiting 89 and 85% spore germination of *P. oryzae* and *H. oryzae*, respectively at 1000 ppm concentration.

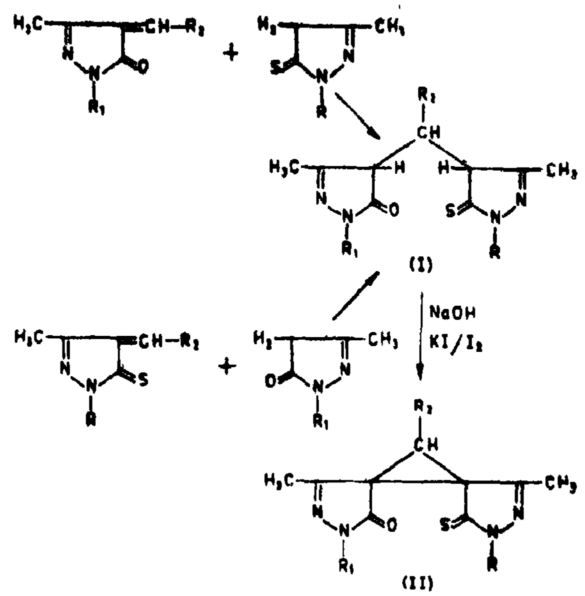


TABLE 1 – PHYSICAL AND FUNGICIDAL DATA OF 1-ARYL-1-(1-PHENYL-3 METHYL-2-PYRAZOLIN-5-ONE)-1-(1′-PHENYL-3′-METHYL-2′-PYRAZOLIN-5′-THIONE)-METHANE (I)

R = C_6H_5 (1 – 19), R_1 = C_6H_5 (1 – 10), H (11-19)

Compd. no.	R_2	M. p. °C	Sulphur %; Found (Calcd.)	Yield %	Germination inhibition % at 1000 ppm *P. oryzae*/*H. oryzae*
1.	C_6H_5	132	7.20 (7.07)	50	61/58
2.	o-OHC_6H_4	55	6.15 (6.83)	48	89/85
3.	m-OHC_6H_4	73	6.20 (6.83)	45	52/48
4.	p-OHC_6H_4	70	6.45 (6.83)	45	57/70
5.	o-$NO_2C_6H_4$	95	6.05 (6.43)	55	80/61
6.	m-$NO_2C_6H_4$	185	6.65 (6.43)	50	48/41
7.	p-$NO_2C_6H_4$	140	6.89 (6.43)	55	44/53
8.	$OCH_3C_6H_4$	75	5.94 (6.63)	45	39/53
9.	$OHOCH_3C_6H_3$	310	5.85 (6.42)	48	45/57
10.	C_4H_3O	100	7.02 (7.23)	45	68/28
11.	C_6H_5	120	9.85 (8.51)	50	45/57
12.	o-OHC_6H_4	140	9.92 (8.16)	55	58/87
13.	m-OHC_6H_4	240	9.82 (8.16)	50	47/37
14.	p-OHC_6H_4	210	9.45 (8.16)	45	51/53
15.	o-$NO_2C_6H_4$	170	8.98 (7.60)	50	73/60
16.	m-$NO_2C_6H_4$	280	8.68 (7.60)	45	35.51
17.	p-$NO_2C_6H_4$	137	8.86 (7.60)	48	79/37
18.	$OCH_3C_6H_4$	84	8.05 (7.88)	45	45/54
19.	$OHOCH_3C_6H_3$	73	8.10 (7.58)	40	37/53

TABLE 2 – PHYSICAL AND FUNGICIDAL DATA OF CYCLOPROPANE DERIVATIVES OF 1-ARYL-1-(1-PHENYL-3-METHYL-2-PYRAZOLIN-5-ONE)-1-(1′-PHENYL-3′-METHYL-2′-PYRAZOLIN-5′-THIONE)-METHANE (II)

$R = C_6H_5$ (1 – 19), $R_1 = C_6H_5$ (1 – 10) H (11 – 19)

Compd. no.	R_2	M. p. °C	Sulphur % ; Found/ (Calcd.)	Yield %	Germination inhibition % at 1000 ppm *P. oryzae*/ *H. oryzae*
1.	C_6H_5	90	8.10 (7.11)	40	54/37
2.	*o*-OHC_6H_4	150	6.32 (6.86)	45	40/33
3.	*m*-OHC_6H_4	160	6.05 (6.86)	40	70/57
4.	*p*-OHC_6H_4	125	6.15 (6.86)	35	39/45
5.	*o*-$NO_2C_6H_4$	192	6.23 (6.46)	45	67/63
6.	*m*-$NO_2C_6H_4$	90	6.96 (6.46)	40	43/40
7.	*p*-$NO_2C_6H_4$	170	6.20 (6.46)	42	47/35
8.	$OCH_3C_6H_4$	121	6.95 (6.66)	50	41/44
9.	OH-3-$OCH_3C_6H_3$	110	7.03 (6.45)	45	40/42
10.	C_4H_3O	75	7.00 (7.27)	40	61/60
11.	C_6H_5	105	8.25 (8.55)	45	37/32
12.	*o*-OHC_6H_4	177	9.98 (8.20)	40	57/52
13.	*m*-OHC_6H_4	120	9.87 (8.20)	38	42/43
14.	*p*-OHC_6H_4	190	9.63 (8.20)	35	47/39
15.	*o*-$NO_2C_6H_4$	155	8.09 (7.63)	45	40/38
16.	*m*-$NO_2C_6H_4$	300	8.17 (7.63)	42	53/41
17.	*p*-$NO_2C_6H_4$	240	8.23 (7.63)	40	51/53
18.	$OCH_3C_6H_4$	125	8.21 (7.92)	35	38/40
19.	C_4H_3O	73	8.09 (8.42)	42	28/43

Out of 19 cyclopropane derivatives (Table 2), compounds no. 3, 5 and 10 showed considerable activity against both the pathogens. Encouraging results were not noticed with the rest of the compounds. So it is concluded that the formation of cyclopropane ring in these compounds retards the activity markedly.

The relevant data on elemental analysis, m.p. and fungitoxicity results are presented in Table 1 and 2.

Experimental

1-Aryl-1-(1-phenyl-3-methyl-2-pyrozolin-one)-1-(1′-phenyl-3′-methyl-2′-pyrozolin-5′-thione) methane (**I**) : Method A : 1-Phenyl-3-methyl-4-monoarylidene-5-pyrozolone (0.01 mol) was taken in ethanol (20 ml) and to it an alkaline solution of 1-phenyl-3-methyl-2-pyrazolin-5-thione (0.01 mol) was added dropwise. The mixture was refluxed for 4 h over water bath. Then excess alcohol was evaporated off and the resulting mixture acidified with cold dil. HCl. A light pink coloured compound precipitated out was filtered, washed with distilled water and finally dried in vacuum. Crystallisation of the solid from ethanol yielded light pink crystals (70%), m.p. 132°. The compound was soluble in 10% NaOH solution and gave colouration with alcoholic $FeCl_3$.

Method B : A mixture of 1-phenyl-3-methyl-4-mono-arylidene-2-pyrozolin-5-thione (0.01 mol) in ethanol (20 ml) and 1-phenyl-3-methyl-5-pyrazolone (0.01 mol) in 10% NaOH solution (25 ml) was refluxed for 4 h over water bath. The excess of ethanol was evaporated and the mass was acidified with cold dil. HCl. A light pink coloured solid precipitated out was filtered, washed with distilled water, dried in vacuum and finally crystallised from ethanol to yield light pink crystals (75%), m.p. 132°. The compound was soluble in 10% NaOH solution and gave red colouration with alcoholic $FeCl_3$.

Cyclopropane derivatives of 1-aryl-1-(1-phenyl-3-methyl-2-pyrazolin-5-one)-1-(1′-phenyl-3′-methyl-2′-pyrazolin-5′-thione) methane (**II**) : Compound **I** (5 g) was dissolved in 20% NaOH solution (25 ml) and to it a saturated solution of iodine in potassium iodide (20 ml) was added dropwise with constant stirring for 2 h. The brown precipitate thus obtained was filtered and washed with 20% sodium thiosulphate solution and then with distilled water and finally crystallised from ethanol to yield light brown crystals (50%), m.p. 90°. The compound was insoluble in 10% NaOH solution and gave no colouration with alcoholic $FeCl_3$ solution.

Acknowledgement

The authors are thankful to the Director, Central Rice Research Institute, Cuttack for providing necessary facilities to carry out the fungicidal tests.

References

1. B. NANDA, B. TRIPATHY, S. PADMANAVAN and A. S. MITTRA, *J. Indian Chem. Soc.*, 1975, **52**, 538.
2. A. NAYAK, S. DAS, C. R. MISRA and A. S. MITTRA, *J. Indian Chem. Soc.*, 1977, **54**, 485.
3. A. NAYAK and A. S. MITTRA, *J. Indian Chem. Soc.*, 1978, **55**, 593.
4. A. NAYAK and A. S. MITTRA, *J. Indian Chem. Soc.*, 1980, **57**, 643.
5. N. B. DAS and A. S. MITTRA, *J. Indian Chem. Soc.*, 1978, **55**, 907.
6. S. RAO and A. S. MITTRA, *Indian J. Chem., Sect. B*, 1977, **15**, 1062.
7. S. K. MOHANTY, R. SRIDHAR, S. RAO, S. PADMANAVAN and A. S. MITTRA, *Indian J. Chem., Sect. B*, 1977, **15**, 1146.
8. A. MOORE and J. MONTOGOMERY, *J. Promol. Hort. Sci.*, 1938, **15**, 253.

Synthesis and *in vitro* Antibacterial Activity of Substituted Phenoxyacetic Acid Hydrazides

ANIL K. SENGUPTA, M. M. GUPTA
and
ANURAG ATEET GUPTA

Department of Chemistry, University of Lucknow, Lucknow-226 007

Manuscript received 4 October 1982, revised 6 December 1983, accepted 3 May 1984

A number of isatin derivatives are known to be physiologically active and some of them possess antibacterial[1,2] and pesticidal properties[3]. Also hydrazones of isatin have been reported to act as potential antiviral[4] and antibacterial agents[5] apart from other potential biological activities[6,7]. In view of these observations, we synthesised the hitherto unknown class of compounds *viz.* substituted phenoxyacetic acid (1-benzoyl-1,2-dihydro-2-oxo-3*H*-indol-3-ylidene) hydrazide and acetic/benzoic acid (1-benzoyl-1,2-dihydro-2-oxo-3*H*-indol-3-ylidene) (substituted phenoxyacetic acid) hydrazide and tested them for their antibacterial activity.

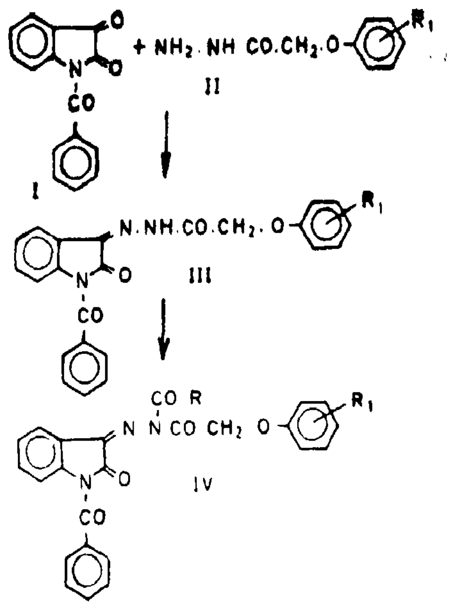
Substituted phenoxyacetic acid hydrazide (II), obtained by the reaction of substituted phenol with ethyl bromoacetate followed by treatment with hydrazine hydrate (99%)[8], has been condensed with 1-benzoyl isatin, obtained from aniline, hydroxylamine and chloral hydrate[9] followed by benzoylation[10], to furnish substituted phenoxyacetic acid (1-benzoyl-1,2-dihydro-2-oxo-3*H*-indol-3-ylidene) hydrazide (IIIa-g) All these compounds have adequately been characterised by means of elemental analyses and the structures of these new compounds were in full agreement with their ir spectral data.

Treatment of IIIa-g with acetic anhydride/benzoylchloride in pyridine yielded acetic/benzoic acid (1-benzoyl-1,2-dihydro-2-oxo-3*H*-indol-3-ylidene) (substituted phenoxyacetic acid) hydrazide (IVa-n). Structures of these compounds were supported by their elemental analyses. Ir spectra showed bands at 1550 (C=N) and 1280, 1060cm^{-1} (CH_2-O-Ar). Further, absence of bands in the region 3000 cm^{-1} onwards confirmed the *N*-substitution of the acyclic $-CO-NH-$ group.

Experimental

M.p.s were taken in open capillary tubes and were uncorrected. Ir spectra (KBr) were recorded on a Perkin-Elmer 137 spectrophotometer.

Substituted phenoxyacetyl hydrazides (IIa-g) were prepared by the reported method[8]. Isatin was prepared[9] from aniline, hydroxylamine and chloral hydrate and the corresponding 1-benzoylisatin (I) by the reported method[10].



*Phenoxyacetic acid (1-benzoyl-1,2-dihydro-2-oxo-3*H*-indol-3-ylidene)hydrazide* **(IIIa)**: A suspension of 1-benzoylisatin (I) (2.51 g, 0.01 mol) with AcOH (2 drops) in ethanol was refluxed, then **IIa** (1.66 g, 0.01 mol) was added to it after a few min and heating continued for about 6 h. The reaction mixture was then allowed to cool and the solid mass thus obtained was filtered and crystallised from ethanol. Other hydrazones (IIb-g) were prepared in a similar manner and are listed in Table 1.

*Acetic acid (1-benzoyl-1,2-dihydro-2-oxo-3*H*-indol-3-ylidene) (phenoxyacetic acid) hydrazide* **(IVa)**: To a solution of **IIIa** (3.99 g, 0.01 mol) in dry pyridine (50 ml) was added acetic anhydride (1.0 g, 0.01 mol). The resulting solution was heated on a steam bath for 4 h. A crystalline solid mass obtained was separated by filtration, washed with $NaHCO_3$ solution followed by ice cold water, and recrystallised from ethanol. Other such derivatives (IVb-n) were prepared in a similar manner (Table 1). While preparing IV(h-n), benzoyl chloride was taken in place of acetic anhydride.

Antibacterial activity: *In vitro* activity of compounds was carried out using the agar diffusion technique[11] against *Bacillus subtilis*, *Bacillus pumilus* and *Staphylococcus aureus*. 5 mm diameter sterilized filter paper disc impregnated with 10 mg ml^{-1} solution of the test compounds was placed on a agar plate seeded with the test organism. The seeded plates were incubated for 24 h at 37 ± 1° and the zone of inhibition of bacterial growth around the disc was then observed. Three replications of each test compound were made and tetracycline-HCl was used as control.

Results and Discussion

The results obtained showed that in the twenty one compounds the presence of *p*-bromo and

TABLE 1 – PHYSICAL PROPERTIES OF HYDRAZONES (IIIa-g AND IVa-n)

Compd. no.	R_1	M.p. °C	Yield %	N% ; Found/ (Calcd.)
R = H				
IIIa	H	221	70	10.61 (10.52)
IIIb	o-CH_3	228	80	10.18 (10.16)
IIIc	m-CH_3	236	76	10.23 (10.16)
IIId	p-CH_3	241	90	10.21 (10.16)
IIIe	p-Cl	248	85	9.61 (9.69)
IIIf	p-Br	226	60	8.95 (8.78)
IIIg	p-NO_2	237	65	13.44 (12.61)
R = CH_3				
IVa	H	185	60	9 65 (9.52)
IVb	o-CH_3	176	55	9.12 (9.23)
IVc	m-CH_3	155	50	9 21 (9.23)
IVd	p-CH_3	165	65	9.26 (9.23)
IVe	p-Cl	178	63	8 65 (8 83)
IVf	p-Br	164	54	8.11 (8.07)
IVg	p-NO_2	195	62	11.56 (11.52)
R = C_6H_5				
IVh	H	208	72	8.12 (8.34)
IVi	o-CH_3	192	65	8.24 (8.12)
IVj	m-CH_3	181	70	8.15 (8.12)
IVk	p-CH_3	201	66	8.17 (8.12)
IVl	p-Cl	208	75	7.45 (7.81)
IVm	p-Br	188	70	7.15 (7.21)
IVn	p-NO_2	210	65	10.12 (10.21)

Satisfactory C and H analysis was obtained.

p-nitro groups in the phenoxy ring [compds. no. III(f,g) and IV(f,g,m,n)] exhibited more pronounced antibacterial activity than rest of the compounds tested. It was further noticed that the introduction of acetyl or benzoyl substituted on acyclic —CO—NH— group effects a decrease in the antibacterial activity. This decrease in the activity is maximum when the benzoyl group is substituted on —CO—NH— (comps. no. IVm, n). Against *S. aureus*, all these six compounds exhibited increased activity, whereas against *B. subtilis* and *B. pumilus*, comparatively lesser antibacterial activity was observed, except compd. no. IVg which showed pronounced antibacterial activity against *B. pumilus*.

Acknowledgement

The authors thank the Head, Department of Chemistry, Lucknow University, for necessary facilities, Dr. Nityanand, Director, C.D.R.I., Lucknow for ir and microanalysis, and Dr. Kurt L. Loening, Director-Nomenclature, Chemical Abstract Service for the nomenclature of the compounds. The authors are grateful to U.G.C. and C.S.I.R., New Delhi for the award of Teacher Research Fellowship (M.M.G.) and Post Doctoral Fellowship (A.A.G.)

References

1. B. TINLAND, *Il Farmaco., Ed. Sci.*, 1976, 31, 888.
2. R. S. VARMA and W. L. NOBLES *J. Med. Chem.*, 1967, 10, 972.
3. A. K. SENGUPTA and A. A. GUPTA, *Indian J. Chem., Sect. B*, 1982, 21, 72.
4. J. BORYSIEWICZ, *Chem. Abstr.*, 1980, 93, 106811.
5. A. K. SENGUPTA and A. A. GUPTA, *J. Chem. Soc. Pak.*, submitted for publication.
6. I. ZGORNIAK-NOWOSIELSKA, A. GATKIEWICZ, A. VECTENSTEDT and I. BELADI, *Acta Virol.*, 1980, 24, 439 (*Chem. Abstr.*, 1981, 94, 76764).
7. E. TONEW, H. P. SCHROEER, B. FAHLBUSCH, L. HEINISCH and H. WILLITZER, *Chem. Abstr.*, 1980, 93, 197564.
8. A. K. SENGUPTA, K. AVASTHI and P. K. SETH, *J. Indian Chem. Soc.*, 1975, 52, 1084.
9. C. S. MARREL and C. S. HIERS in "Organic Synthesis, Collected Volume 1", ed. H. GILMAN, John Wiley, New York, 1941, p. 327.
10. LIEBERMANN and KRAUSE, *Chem. Ber.*, 1907, 40, 2492.
11. R. S. VARMA and W. L. NOBLES, *J. Pharm. Sci.*, 1968, 57, 1801.

Synthesis and Antifungal Activity of Aryloxyacetyl Hydrazones of Fluoro Aralkyl/Diaryl Ketones

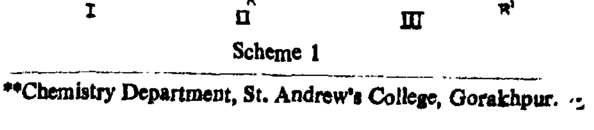
R. S. SHARMA, R. B. PATHAK** and S. C. BAHEL*

Chemistry Department, Gorakhpur University, Gorakhpur-273 001

Manuscript received 18 December 1982, revised 20 January 1984, accepted 3 May 1984

KHAN and Bahel[1] prepared fluorinated aryl hydrazones as fungicides. The —CONH—N=C= moiety of hydrazones imparts biological activities to such compounds[2]. Various hydrazones have been reported useful as fungicides[3,4], bactericides[5] and psychotropics[6]. In view of these observations, we have prepared the title hydrazones which might display significant activity due to presence of fluorine and an aryloxyacetyl moiety.

The hydrazones (III) have been obtained by the condensation of aryloxyacetyl hydrazines (I) and fluorinated aralkyl/diaryl ketones (II) (Scheme 1).



Scheme 1

**Chemistry Department, St. Andrew's College, Gorakhpur.

TABLE 1 – FUNGICIDAL DATA OF FLUOROARALKYL/DIARYL-KETO-ARYLOXYACETYL HYDRAZONES (III)

Concn. / Compd no.	Average % inhibition after 96 h*					
	A. niger			*H. oryzae*		
	1000 ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm
1	65.5	52.0	37.4	75.4	49.2	39.1
2	59.4	42.1	31.2	64.4	42.0	30.7
3	67.1	49.2	35.0	74.1	52.2	36.2
5	74.4	46.3	38.8	73.2	54.1	40.3
6	70.8	51.5	32.0	65.6	47.1	31.8
8	70.6	48.1	32.7	69.2	42.8	33.6
9	55.4	38.6	28.9	60.2	42.1	30.4
11	56.2	36.1	26.8	58.2	34.7	25.5
12	58.3	42.1	24.5	60.1	36.9	24.3
13	61.8	39.7	29.3	64.3	44.8	30.5
14	73.1	38.0	28.0	61.1	46.8	27.0
BLITOX 50 WP	94.0	81.8	75.0	96.4	91.2	81.0

* Three replications in each case.

The structures of these compounds were supported by elemental analyses, ir and nmr spectra.

Experimental

All the melting points are uncorrected. Ir spectra (KBr) of the compounds were taken in Perkin-Elmer spectrophotometer. Nmr spectra of the compounds were recorded in $CDCl_3$ solution.

Aryloxyacetyl hydrazines (I): These were prepared by the method of Conti[7].

Fluorinated aralkyl/diaryl ketones (II): These were prepared by the method of Buu-Hoi and Xuong[8].

Fluoroaralkyl/diaryl-keto-aryloxyacetylhydrazones (III): To a hot methanolic solution of aryloxyacetylhydrazine (0.01 *M*) a methanolic solution of fluoroaralkyl/diaryl ketone (0.01 *M*) was added dropwise with vigorous shaking. Few drops of glacial acetic acid were added and the solution refluxed on steam bath for 4 h and cooled. The solid separating out was filtered, washed and recrystallised from aqueous ethanol to yield the product, Compd. no. 1, R = 4-Cl-3-CH_3.C_6H_3, R'=C_2H_5, (52%), m. p. 166°; ν_{max} 3220 (broad -NH-), 1685 (-CO.NH-), 1600 (C=N), 1100 (C-F), 1050 (-C-O-C-) and 750 cm^{-1} (C-Cl) Compd. no. 2, R=2,6-$(CH_3)_2$.C_6H_3, R'=C_2H_5, (53%), m p. 81°. Compd. no. 3, R=3,5-$(CH_3)_2$ C_6H_3, R'=C_2H_5, (87%), m.p. 128-129°. Compd. no. 4, R=2,4-$(CH_3)_2$.C_6H_3, R'=C_2H_5, (56%), m p. 84°. Compd. no. 5, R=4-Cl-3-CH_3.C_6H_3, R'=C_3H_7, (66%), m.p. 154°. Compd. no. 6, R=2,6-$(CH_3)_2$.C_6H_3, R'=C_3H_7, (74%), m.p. 180°; ν_{max} 3250 (road -NH), 1740 (-CO.NH-), 1650 (C=N), 1035 (-C-O-C-) and 745 cm^{-1} (1,2,3-trisubstituted benzene). Compd. no. 7, R=3,5-$(CH_3)_2$.C_6H_3, R'=C_3H_7, (57%), m.p. 65°. Compd. no. 8, R=2,4-$(CH_3)_2$.C_6H_3, R' = C_3H_7, (72%), m p. 93°. Compd. no. 9, R=4-Cl-3-CH_3.C_6H_3, R'=C_6H_5, (77%), m.p. 101°. Compd. no. 10, R=2,6-$(CH_3)_2$.C_6H_3, R'=C_6H_5, (76%), m.p. 60°. Compd. no. 11, R =3,5-$(CH_3)_2$, C_6H_3, R'=C_6H_5, (95%), m.p. 88°; ν_{max} 3200 (broad -NH), 1680(-CO.NH-), 1650(C=N), 1130 (C-F) and 1035 cm^{-1} (-C-O-C-); δ 1.7 (S, 9H, CH_3), 2.8 (S, 2H, -CO.CH_2), 6.4 (b, 1H, =N.NH), 7.8 (m, 11H, aromatic protons). Compd. no. 12, R= 2,4-$(CH_3)_2$.C_6H_3, R'=C_6H_5, (97%), m.p. 100°. Compd. no. 13. R = 3,5-$(CH_3)_2$.C_6H_3, R' = 4-Cl.C_6H_4, (91%), m.p. 112°. Compd. no. 14, R= 2,4-$(CH_3)_2$.C_6H_3, R'=4-Cl.C_6H_4, (70%), m.p. 162°. The elemental analyses of the above compounds were found to be within satisfactory limits.

Fungicidal screening: Eleven compounds were evaluated for their antifungal activity against *A. niger* and *H. oryzae* by agar plate technique[9] at concentrations 1000, 100 and 10 ppm. The fungicidal activity displayed by compounds has been given in Table 1. A commercial fungicide BLITOX 50 WP was also tested under similar conditions to compare the result.

Results and Discussion

Most of the compounds have significant fungitoxicity at 1000 and 100 ppm against both the fungi but their fungicidal action decreased upon dilution. Although the compounds no. 1, 3, 5, inhibit > 35% of the growth of both the test organisms even at 10 ppm, the results are not so spectacular as one may expect due to the presence of fluorine and aryloxyacetyl moiety.

It is further revealed that compounds with 4-chloro-3-methyl moiety are relatively more potent. Compounds having 3,5-dimethyl groups are more fungitoxic than those with methyl groups at other positions in benzene nucleus. In general, fluorobenzophenone hydrazones are less fungitoxic than the corresponding fluoropropiophenone/butyrophenone hydrazones.

Acknowledgement

Authors are thankful to Prof. R. P. Rastogi, Head, Chemistry Department, Gorakhpur University

for laboratory facilities. One of the authors (R.S.S.) is grateful to Y. D. Post-graduate College, Lakhimpur-Kheri for granting leave and to U.G.C., New Delhi for the award of Teacher Fellowship.

References

1. R. H. KHAN and S. C. BAHEL, *Agric. Biol. Chem.*, 1976, **40**, 2481.
2. L. GIAMMANO, *Ann. Chim.*, 1961, **55**, 175 (*Chem. Abstr.*, 1961, **55**, 18725).
3. S. ALKIRA and L. MASUMI, *Yakugaku Zasshi*, 1965, **85**, 418 (*Chem. Abstr.*, 1965, **63**, 5640).
4. R. B. PATHAK and S. C. BAHEL, *J. Antibact. Antifung. Agents*, 1981, **9**, 9.
5. S. BAHADUR, A. K. GOEL and R. S. VARMA, *J. Indian Chem. Soc.*, 1975, **52**, 843.
6. K. SASAJIMA, K. ONO, H. NAKAO, I. MARAYAMA, S. KATAYAMA, S. INABA and H. YAMAMOTO, Ger. Offen. 2536164/1976 (*Chem. Abstr.*, 1976, **84**, 164631).
7. L. CONTI, *Boll. Sci. Fac. Chim. Ind. Bologna*, 1964, **22**, 13 (*Chem. Abstr.*, 1964, **61**, 4253).
8. NG. PH. BUU-HOI and N. D. XUONG, *J. Chem. Soc.*, 1953, 386.
9. J. G. HORSFALL, *Bot. Rev.*, 1945, **11**, 257.

Synthesis and Mercuration of Some New 2-Arylimino-4-oxazolidones as Pesticides

J. P. NATH and D. N. ROUT

Department of Chemistry, Bhadrak College, Bhadrak-756 100

and

S. C. SATRUSALLYA*, B. K. PATTNAYAK

and

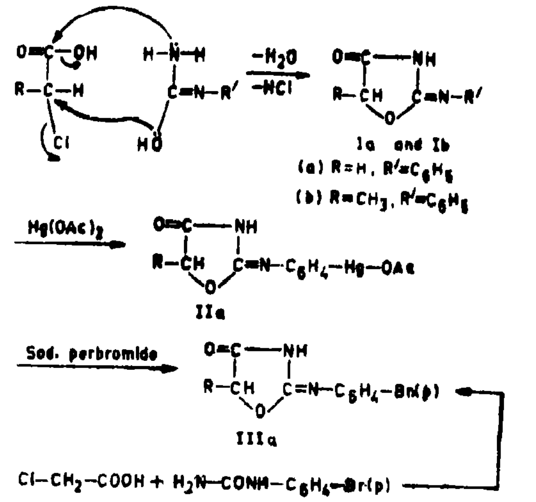
G. N. MAHAPATRA

Department of Chemistry, Ravenshaw College, Cuttack-753 003

Manuscript received 29 March 1983, revised 13 February 1984, accepted 3 May 1984

CHEMISTRY[1] and wide range of pharmacological[2-4] properties of oxazolidones have been cited in the literature. In the present work an attempt has been made to synthesise some new 2-arylimino-4-oxazolidones (**Ia** and **Ib**) by condensing different monoaryl ureas with chloroacetic acid and α-chloropropionic acid separately in presence of anhydrous sodium acetate in absolute ethanol medium.

Structure Ia of the compound has been established from the characteristic ir peaks at 1560 (N–C–O), 3260 (NH) and 1742 cm^{-1} (C=O five membered β-lactum ring[5]), and pmr peaks at τ 5.8 (2H, s), 5.2 (1H, br, s) and 2.6 (4H, s) due to $-CH_2-$ at 5-position of the ring, –NH–, and aromatic protons, respectively. Structure **Ib** was confirmed from ir peaks at 1560 (N–C–O), 3260 (NH) and 1742 cm^{-1} (=C=O), and pmr peaks at τ 5.6 (1H, s), 8.2 (3H, m), 5.2 (1H, br, m) and 2.6 (4H, s) assigned to –CH– at 5-position of the ring, CH_3- at C_5 position, –NH– and aromatic protons, respectively with tetramethylsilane as internal standard. It was further substantiated from the reported[6] sulphur analogue, 2-arylimino-4-thiazolidones under the similar experimental condition.



Further, **Ia** and **Ib** were mercurated by one equivalent of mercuric acetate with a view to enhance their pesticidal activity. Acetoxymercuri group usually enters into the *para* position[7] of *N*-phenyl nucleus if it is free, otherwise occupies the *ortho* position of the same nucleus. The position of acetoxymercuri group is further justified from the fact that 2-imino-4-oxazolidone synthesised from urea and chloroacetic acid is never mercurated under these experimental conditions. The final evidence for the position of acetoxymercuri group comes from the following observations.

Monoacetoxymercuri compound, **IIa** was treated with sodium perbromide to yield compound **IIIa**, which was identical with 2-(*p*-bromophenyl)-imino-4-oxazolidone synthesised independently from *p*-bromophenylurea and chloroacetic acid. The identity of the two compounds were established through superimposable ir curve, identical R_f value by tlc and undepressed m.m.p.

Experimental

2-Phenylimino-4-oxazolidone (**Ia**): Phenyl urea (0.05 mol) was refluxed with chloroacetic acid (0.05 mol) in presence of sodium acetate (3.5 g) in absolute ethanol (25 ml) on a boiling water bath for 20 h. The reaction mixture was then poured into cold water and the precipitate washed with hot water. It was crystallised from rectified spirit to yield the product (80%), m.p. 207° (Found : N, 15.70. $C_9H_8O_2N_2$ requires N, 15.90%).

2-(p-Acetoxymercuriphenyl) imino-4-oxazolidone (**IIa**): 2-Phenylimino-4-oxazolidone (0.01 mol) in acetic acid-ethanol (1 : 1, 10 ml) was treated with a solution of mercuric acetate (0.01 mol) in acetic

TABLE 1—PHYSICAL AND PESTICIDAL DATA OF VARIOUS 2-ARYLIMINO-4-OXAZOLIDONES (I)* AND THEIR ACETOXYMERCURI DERIVATIVES (II)*

Sl. no. R′	Oxazolidones (I)* M.p. °C	N% Found/ (Calcd.)	Activity: Fungicidal[a] P. oryzae	Bactericidal[b] E. coli	Bactericidal[b] S. aureus	Hg Derivatives (II)* M.p. °C	Hg % Found/ (Calcd.)	Activity: Fungicidal[a] P. oryzae	Bactericidal[b] E. coli	Bactericidal[b] S. aureus
R = H										
1. C_6H_5	207	15.70 (15.90)	5.0	–	–	242	45.98 (46.15)	3.0	+	+
2. *o*-Cl.C_6H_4	220	13.12 (13.30)	3.2	+	+	>250	42.60 (42.76)	1.5	+	+
3. *m*-Cl.C_6H_4	185	13.10 (13.30)	2.5	+	+	195_d	42.55 (42.76)	1.5	+	+
4. *p*-Cl.C_6H_4	240	13.09 (13.30)	2.5	+	+	>250	42.62 (42.76)	1.5	+	+
5. *p*-Br.C_6H_4	>250	10.75 (10.98)	3.5	+	+	>250	38.82 (39.05)	2.2	–	+
6. *o*-$CH_3O.C_6H_4$	163	13.35 (13.59)	4.5	–	–	197	43.03 (43.17)	2.5	–	+
7. *m*-$CH_3O.C_6H_4$	141	13.40 (13.59)	4.0	–	–	185	43.05 (43.17)	2.8	–	+
8. *p*-$CH_3O.C_6H_4$	211	13.37 (13.59)	4.5	–	–	>250	43.00 (43.17)	3.0	–	+
9. *o*-$CH_3.C_6H_4$	235	14.51 (14.73)	5.5	+	–	>250	44.58 (44.71)	3.5	+	+
10. *m*-$CH_3.C_6H_4$	210	14.53 (14.73)	5.0	+	+	238	44.49 (44.71)	3.5	+	+
11. *p*-$CH_3.C_6H_4$	242	14.56 (14.73)	5.0	–	–	>250	44.56 (44.71)	3.0	+	+
R = CH_3										
12. C_6H_5	223	14.51 (14.71)	6.5	–	–	>250	44.54 (44.71)	4.0	+	+
13. *o*-Cl.C_6H_4	225	12.25 (12.47)	4.0	–	+	>250	41.35 (41.52)	2.5	+	+
14. *m*-Cl.C_6H_4	216_d	12.23 (12.47)	4.0	+	+	>250	41.40 (41.52)	2.5	+	+
15. *p*-Cl.C_6H_4	185	12.26 (12.47)	3.5	+	+	232	41.42 (41.52)	2.5	+	+
16. *p*-Br.C_6H_4	>250	10.19 (10.40)	4.4	+	+	>250	37.85 (38.02)	3.0	+	–
17. *o*-$CH_3O.C_6H_4$	190	12 48 (12.72)	4.8	–	–	201	41.75 (41.91)	3.5	–	–
18. *m*-$CH_3O.C_6H_4$	160	12.50 (12.72)	5.0	–	–	195_d	41.80 (41.91)	4.5	+	+
19. *p*-$CH_3O.C_6H_4$	>250	12.51 (12.72)	5.2	–	+	>250	41.78 (41.91)	3.2	+	+
20. *o*-$CH_3.C_6H_4$	223	13.51 (13.72)	5.5	–	–	>250	43.25 (43.36)	3.5	–	–
21. *m*-$CH_3.C_6H_4$	195	13.50 (13.72)	5.0	–	–	230	43.27 (43.36)	3.5	+	+
22. *p*-$CH_3.C_6H_4$	246	13.48 (13.72)	6.0	–	–	>250	43.23 (43.36)	4.0	–	–

* Yield 60-80%, m.sp. uncorrected, satisfactory elemental analyses.
a – ppm for 50% spore germination.
b – At 100 ppm.
+ Active.
– Inactive.

acid (1*N*, 20 ml). The mixture was stirred well and kept overnight at room temperature. The resulting precipitate was filtered, washed with hot water and then with acetic acid-ethanol solution to yield the product (70%), m.p. 242° (Found : Hg, 45.98. $C_{11}H_{10}O_4N_2Hg$ requires Hg, 46.15%).

Fungicidal activity : The compounds were screened for their fungicidal activity against *Pyricularia oryzae* (*CaV*) by the method of Montegomery and Moore[6], and the results are given in Table 1. The results may be generalised as follows ;

(i) Almost all the compounds showed promising antifungal activity.

(ii) Presence of halogen, especially chloride on the *N*-phenyl ring augments the antifungal activity remarkably.

(iii) The compounds with R=H are more active than those with R=CH_3.

(iv) Acetoxymercuri derivatives, **IIa** and **IIb** are in general about two times more active than

the corresponding non-mercurated oxazolidones (Ia and Ib).

Bactericidal activity: The bactericidal activity of synthesised compounds, both mercurated and non-mercurated ones have been assayed against two common pathgenic bacteria, *E. coli* and *S. aureus*, separately by Rideal-Walker serial drop dilution method[9]. The results are given in Table 1. Both the bacteria are equally sensitive towards the compounds Ia and Ib at 100 ppm level.

Acknowledgement

The authors are grateful to the B.S.I.R., Government of Orissa for financial assistance. One of the authors (S.C.S.) is grateful to the U.G.C., New Delhi for the award of a Teacher Fellowship.

References

1. J. W. CORNFORTH, "Heterocyclic Compounds", John Wiley, New York, 1956, Vol. 5.
2. I. D. DRUTTA and C. H. BUDEANU, *Chem. Abstr.*, 1973, 79, 137098.
3. R. S. VERMA, *J. Prakt. Chem.*, 1973, 315, 350.
4. R. B. FUGITT and L. C. MARTINELLI, *J. Pharm. Sci.*, 1973, 62, 613 (*Chem. Abstr.*, 1973, 79, 5321).
5. R. M. SILVERSTEIN, G. C. BASSLER and T. C. MORRILL, "Spectroscopic Identification of Organic Compounds", John Wiley, New York, 1974, p. 107.
6. M. K. ROUT and G. N. MAHAPATRA, *J. Am. Chem. Soc.*, 1955, 77, 2427.
7. G. N. MAHAPATRA and M. K. ROUT, *J. Indian Chem. Soc.*, 1955, 32, 715.
8. H. B. S. MONTGOMERY and M. H. MOORE, *J. Pomol. Hort. Sci.*, 1938, 15, 253.
9. S. RIDEAL and J. F. A. WALKER, *J. R. Sanit. Inst. London*, 1903, 24, 424.

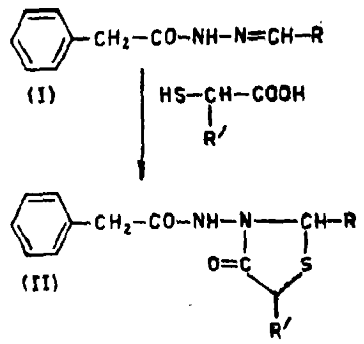
Studies on 4-Thiazolidinones as Antibacterial Agents

S. J. SHAH, S. R. SHAH, N. C. DESAI and K. A. THAKER

University Department of Chemistry, Bhavnagar University, Bhavnagar-364 002

Manuscript received 30 January 1984, accepted 26 May 1984

PHENYLACETIC acid have been known to be active as bactericidal and fungicidal agent. Thiazolidinone derivatives are well known biological active compounds[1-6]. Several substituted thiazolidinones were found to possess anaesthetic, anticonvulsant and sedative properties[7,8]. Besides, compounds having N−C−S grouping have antitubercular[9], antiradiation[10], hematocidal[11] and antibacterial[12] activities. In view of the varied physiological activities of thiazolidinone derivatives several thiazolidinone derivatives have been prepared (II) by the cycloaddition of thioglycollic and thiomalic acid with different hydrazones (Schiff's base).



where R′ = H and
R′ = −CH₂.COOH

Experimental

Phenylacetylhydrazines: These were prepared by the reported method[13].

Hydrazones (I): A mixture of phenylacetylhydrazine and aromatic aldehyde (0.01 mol each) in ethanol (30 ml) and piperidine (3-4 drops) was refluxed on water bath for 1 h. The reaction mixture was cooled, the separated solid was filtered and the product (I) recrystallised from ethanol. Melting points, yield and antibacterial activity of (I) are given in Table 1.

TABLE 1 – HYDRAZONES (I)

Sl. no.	R	M.p. °C	Antibacterial activity *E. coli*	*S. aureus*
1.	$-C_6H_5$	148	–	–
2.	$-2.OH.C_6H_4$	187	–	+
3.	$-4.OCH_3.C_6H_4$	166	+	+
4.	$-5.Br.2.OH.C_6H_3$	198	+	+ +
5.	$-4.NO_2.C_6H_4$	197	–	–
6.	$-3-NO_2.C_6H_4$	183	–	–
7.	$-4.Cl.C_6H_4$	153	–	+
8.	$-3,4-CH_2(O)_2-C_6H_3$	209	–	+
9.	$-4.OH.3.OCH_3.C_6H_3$	135	+	+
10.	$-3,4-di(OCH_3)_2.C_6H_3$	168	+	+
11.	$-4.OH.C_6H_4$	204	–	–
12.	$-4.CH_3.C_6H_4$	137	–	–

C, H, N analyses within ±0.5% theoretical values.
Yield 65 – 75%.
+ = Zone dia. <20 mm.
+ + = Zone dia. >20 mm.
– = No inhibitory zone.

4-Thiazolidinone (II): Method A. A mixture of appropriate hydrazone (I) (0.01 mol) and thioglycollic acid (0.015 mol) in dry benzene (30 ml) was refluxed for 8 h. Excess solvent and thioglycollic acid was removed under vacuum. The residue was washed thoroughly with $NaHCO_3$ solution and water, dried, and the product (II) crystallised from ethanol (95%).

Method B. A mixture of hydrazone (I) and thiomalic acid (0.01 mol each) was condensed in presence of anhydrous zinc chloride (0.5 g) at 160° for 2 h. The temperature was raised to 180° for 30 min, and the product dissolved in sodium bicarbonate (4 *N*) solution and filtered. The filtrate was

TABLE 2—4-THIAZOLIDINONES (II)

Sl. no.	R	R′	M.p. °C	Antibacterial activity E. coli	Antibacterial activity S. aureus
1.	$-C_6H_5$	H	160	–	+
2.	$-2.OH.C_6H_4$	H	178	–	+ +
3.	$-4.OCH_3.C_6H_4$	H	175	+	+
4.	$-5.Br.2.OH.C_6H_3$	H	218	+	+ +
5.	$-4.NO_2.C_6H_4$	H	150	–	–
6.	$-3NO_2.C_6H_4$	H	115	–	–
7.	$-4.Cl.C_6H_4$	H	118	+	+
8.	$-4.CH_3.C_6H_4$	H	125	–	+
9	$-4.OH.3.OCH_3.C_6H_3$	H	176	+	+ +
10.	$3,4-CH_2.(O)_2.C_6H_3$	H	160		
11.	$-4OH.C_6H_4$	H	215	–	–
12.	$-3,4-di(OCH_3).C_6H_3$	H	220	+	+
13.	$-C_6H_5$	$-CH_2.COOH$	116	+	+
14.	$-2-OH.C_6H_4$	$-CH_2.COOH$	159	+	+ +
15.	$-4.OCH_3.C_6H_4$	$-CH_2.COOH$	104	+ +	+ +
16.	$-5.Br.2OH.C_6H_3$	$-CH_2.COOH$	129	–	–
17.	$-4-NO_2.C_6H_4$	$-CH_2.COOH$	173	–	+
18.	$-3.NO_2.C_6H_4$	$-CH_2.COOH$	175	–	+
19.	$-4.Cl.C_6H_4$	$-CH_2.COOH$	105	–	+
20.	$-4.CH_3.C_6H_4$	$-CH_2.COOH$	108	+	+ +
21.	$-4.OH.3OCH_3.C_6H_3$	$-CH_2.COOH$	120		
22.	$3,4-CH_2.(O)_2.C_6H_3$	$-CH_2.COOH$	177	+	+
23.	$-4.OH.C_6H_4$	$-CH_2.COOH$	115	–	–
24.	$-3,4-di(OCH_3)C_6H_3$	$-CH_2.COOH$	110	+	+ +

C, H, N analyses were within ±0.5% theoretical values. Yield 55-60%.
Other notations same as in Table 1.

reprecipitated with dilute hydrochloric acid and the product (**II**) crystallised from ethanol (95%). Melting point, yield and bacterial activity of **II** are given in Table 2.

Antibacterial activity: The compounds **I** and **II** were tested for antibacterial activities by nutrient agar plate diffusion technique, dimethyl formamide used as solvent and the compounds found to be active against *E. coli* and *S. aureus* in various concentrations.

Results and Discussion

The structure of the thiazolidinones were elucidated on the basis of ir spectral data. Schiff bases generally give a strong sharp band at 1630-1615 cm^{-1} (C=N stretch). This band is lost in the formation of thiazolidinones and strong bands at 1750 and 1760 cm^{-1} were characteristic for the carbonyl stretching frequency for thiazolidinone ring system.

It has been observed that in the primary screening of bactericidal activity, the *para* position of phenyl is more potent than *ortho* and *meta*. It has also been observed that introduction of bromine in the phenyl ring increases the activity of 4-thiazolidinones.

Acknowledgement

The authors thank C.S.I.R., New Delhi and Bhavnagar University for research scholarships (S.R.S. and S.J.S.) and Dr. S. B. Trivedi, Director, Tuberculosis Research Centre, Amargadh for preliminary antibacterial testing.

References

1. W. J. DORAN and H. A. SHONLE, *J. Org. Chem.*, 1938, **3**, 193.
2. L. C. CHEMOY, R. R. SMITH and S. B. BLINKHBY, *J. Am. Chem. Soc.*, 1949, **71**, 61.
3. G. L. WILLEY, *Br. J. Pharmacol.*, 1955, **10**, 466.
4. R. R. ASTIK, J. N. ACHARYA and G. B. JOSHI, *J. Indian Chem. Soc.*, 1976, **53**, 272.
5. D. R. PATEL, P. S. SATPATHI, P. B. PATEL and J. J. TRIVEDI, *J. Inst. Chem., Calcutta*, 1976, **48**, 305.
6. P. HERY, *Br. J. Pharmacol.*, 1952, **7**, 117.
7. A. R. SURRY, *J. Am. Chem. Soc.*, 1949, **71**, 3354.
8. H. D. TRAUTMAN and L. M. LONG, *J. Am. Chem. Soc.*, 1948, **70**, 3436.
9. H. K. SHUKLA, R. R. ASTIK and K. A. THAKER, *J. Indian Chem. Soc.*, 1981, **58**, 1182.
10. G. O. HENDRICKS, *J. Med. Pharm. Chem.*, 1965, **8**, 762.
11. J. R. GEISY, French Pat., 1395069, 1965 (*Chem. Abstr.*, 1965, **63**, 6936).
12. N. C. DESAI, R. R. ASTIK and K. A. THAKER, *J. Indian Chem. Soc.*, 1982, **59**, 771.
13. L. CONTI, *Bull. Sci. Fac. Chim. Ind. Bologna*, 1964, **22**, 13 (*Chem. Abstr.*, 1964, **61**, 4253).

Polyphenolic Constituents of *Rhus mysorensis leaves*

M. SARADA* and D. ADINARAYANA

Department of Chemistry, Sri Venkateswara University, Tirupati-517 502

Manuscript received 9 November 1982, accepted 25 March 1984

RHUS mysorensis (Heyne) (family Anacardiaceae), a thorny shrub distributed in Deccan hill country was not examined earlier for its flavonoid constituents. The present work deals with the chemical examination of *R. mysorensis* leaves. The isolation

* 6-32, S. V. Nagar, Tirupati-517 502.

of these flavonoids along with their 3-*o*-rhamnosides and a biflavonoid, shows that the leaves of *R. mysorensis* is enriched with flavonoids and flavonoid glycosides in major amounts.

Experimental

1.5 kg shade dried leaves were successively extracted with light petroleum (b.p. 60-80°), benzene and acetone. The vacuum dried acetone extract on alkali fractionation with (a) 2% Na_2CO_3 and (b) 2% NaOH solution, and neutralisation with concentrated hydrochloric acid yielded a solid mixture containing several flavonoid components.

The three major flavonoids were separated by column chromatography (silica gel) of the ethyl acetate soluble portion of the above mixture using benzene-acetone (2 : 8, 5 : 5, 8 : 2) as eluent. The three flavonoids were purified by preparative paper chromatography using ethanol-acetic acid-water (40 : 13 : 30) as irrigating solvent.

Results and Discussion

The above flavonoids are identified as myricetin, quercetin and kaempferol by R_f value uv and ir, pmr and mass spectra of their acetates. The identity of the compounds was also confirmed by co-tlc using authentic specimens.

The higher R_f band of the solid mixture in ppc was further purified by preparative tlc (silica gel G) with benzene : pyridine : formic acid (40 : 10 : 2) and the major band was cut and eluted with pure methanol and recrystallised. It is identified as a biflavonoid containing two apeginin units joined by a C–O–C linkage as 4′–0–6″ which is identical to hinokiflavone. This is further confirmed by m.p., colour reactions and nmr data compared with an authentic specimen.

The methanol extract separated by column chromatography and the major eluent was evaporated with ethyl acetate. The ethyl acetate insoluble portion was separated and purified by preparative pc (40 : 13 : 30, ethanol-acetic acid-water) gave three flavonoid glycosides which were subjected to various colour reactions, uv flourescence and hydrolysis and characterisation of hydrolytic products. All were found to be 3-*o*-glycosides and the single sugar was rhamnose. The aglycones were identified as myrecitin, quercetin and kaempferol.

The identity of the three glycosides as Myrecetin-3-o-rhamnoside, Quercetin-3-o-rhamnoside, and Kaempferol-3-o-rhamnoside was confirmed R_f m.p. and λ_{max} by direct comparison with authentic samples. All the above compounds are isolated for the first time from this species.

Acknowledgement

The author is thankful to Prof. H. Wagner for various spectra and to U.G.C., New Delhi for Teacher Fellowship.

References

1. "The Flavonoids", eds. J. B. HARBOURNE, T. J. MABRY and H. MABRY, Chapman and Hall, London.
2. J. S. GAMBLE, "Flora of the Presidency of Madras", Botanical Survey of India, Calcutta, Vol. 1.
3. T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, "The Systematic Identification of Flavonoids, Springer-Verlag, New York.
4. T. A. GEISSMAN, "The Chemistry of Flavonoid Compounds", Pergamon Press, London.
5. J. B. HARBOURNE, "The Comparative Biochemistry of Flavonoids", Academic Press, London.

3-(1,1-Dimethylallyl) Xanthyletin from *Murraya koenigii* Spreng

P. BHATTACHARYYA and A. CHAKRABORTY

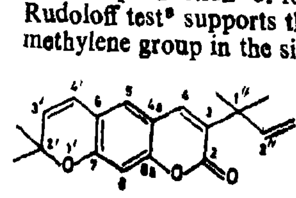
Bose Institute, Calcutta-700 009

Manuscript received 7 July 1983, revised 21 December 1983, accepted 3 May 1984

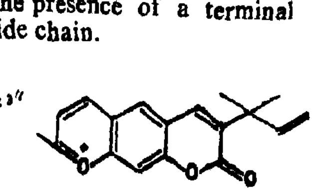
MURRAYA koenigii is known to be the richest source of carbazole alkaloids[1]. Recent investigation reveals the presence of a coumarin from the petroleum ether (b.p. 60-80°) extract of the stem bark of *M. koenigii*. The coumarin has been identified as 3-(*1,1-dimethylallyl*) *xanthyletin* (**I**) which was previously isolated from *Boenninghausenia albifloar*[2].

The compound (**I**) (M^+, 296), m.p. 100° was found homogeneous by tlc and mass spectrometry. It showed λ_{max}. (EtOH) 226, 267, 346 nm (log ε 4.3, 4.3 and 4.1) ; ν_{max}. (KBr) displayed peaks at 1720 (coumarin carbonyl) 1600, 1510 cm^{-1} (aromatic) ; δ (100 MHz, solvent $CDCl_3$, standard Me_4Si), 7.4 (1H, s, C-4), 7.0 (1H, s, C-5), 6.72 (1H, s, C-8), 1.43 (12H, s, four methyl groups), 5.6 (1H, d, J 10 Hz, 3′–H) and 6.3 (1H, d, J 10 Hz, 4′–H). The other signals consisted of an ABX system are (H_A, 5.03, q, J_{AX} 18 Hz ; H_B, 5.08, q, J_{Bx} 10Hz ; H_X, 6.2, q, J_{AB} 1 Hz). The mass spectra of the compound showed a molecular ion peak at m/e 296. The base peak appeared at m/e 281 (M-15) represented by the ionic species (**II**). The other significant peak is at m/e 253 (M-15-28) (M^+, Me-CO).

The production of formaldehyde in Lemieaux-Rudoloff test[3] supports the presence of a terminal methylene group in the side chain.



(I)



(II)

Finally the structure has been determined from ^{13}C nmr (20 MHz, $CDCl_3$) detailed in Table 1.

TABLE 1—^{13}C NMR OF COMPOUND (I)

Carbon no.	ppm	Carbon no.	ppm
2	159.7 s	2′	77.2 s
3	112.9 s	3′	120.8 d
4	145.4 d	4′	124.5 d
4a	118.2 s	1″	40.2 s
5	130.8 d	2″	137.4 d
6	131.5 s	3″	111.9 t
7	154.4 s		
8	103.4 d	1″ < Me, Me	25.9 q*
8a	155.8 s	2′ < Me, Me	28.0 q*

*Values may interchange.

Acknowledgement

The authors express their thanks to Dr. S. C. Bhattacharyya, Director and Prof. A. K. Barua, Chairman, Department of Chemistry for their interest in the work.

References

1. D. P. CHAKRABORTY, *Fortschr. Chem. Org. Naturst.*, 1977, 34, 299.
2. M. N. S. NAYER, M. K. BHAN and V. GEORGE, *Phytochemistry*, 1973, 12, 2073.
3. R. LEMIEUX and E. RUDLOFF, *Can. J. Chem.*, 1955, 33, 1701.

2-Hydroxy-5-carboxy-acetophenone Oxime as an Analytical Reagent for Gravimetric Determination of Palladium

B. L. SHAH and C. M. DESAI*

Department of Chemistry, P. J. Science College, Bardoli-394 601

Manuscript received 8 September 1981, accepted 26 May 1984

2-Hydroxy-5-carboxy-acetophenone oxime (HCAO) has been used as a reagent for gravimetric determination of copper[1] and nickel[2]. The present work describes the use of this ligand for the gravimetric determination of palladium(II). The reagent precipitates palladium ion at 0.8 and is quantitative between *p*H 1.5 to 3.0 and after drying at 110 to 120° the composition of the chelate corresponds to the formula $Pd(C_9H_8O_4N)_2$.

Experimental

Palladium chloride (1.0 g) was dissolved in minimum quantity of hydrochloric acid and the solution was made to 500 ml. with distilled water.

Preparation of reagent: *p*-Hydroxy-benzoic acid was acetylated[3] and the resulting compound *p*-acetoxy-benzoic acid was converted into ketone by the following method[4]. *p*-Acetoxy-benzoic acid (3.0 g, 1 mol) and anhydrous aluminium chloride (7.0 g, 3.3 mol) were intimately mixed and heated on an oil bath at 150 to 155° protected by $CaCl_2$ guard tube for 1 h. The reaction mass was cooled and treated with ice and conc. HCl. The mass was washed and crystallised from ethanol to yield the resulting ketone, 2-hydroxy-5-carboxy-acetophenone[4], m.p. 241°. The oxime was prepared by the reaction of the above ketone with hydroxylamine hydrochloride and sodium acetate in aqueous ethanol Crystallised from ethanol yielded the product, m p. 258°d.

Determination of palladium(II) ion: A known volume (10 ml) of palladium ion solution was diluted to 70-80 ml and *p*H was adjusted to 1.5-2.0 using acetic acid-sodium acetate buffer. The solution was warmed to 60-70° and ethanolic solution of the reagent (1.0%) was added with constant stirring followed by about 10% excess to ensure complete precipitation. The yellow precipitate obtained was digested on water bath (60-80°) for 30 min. It was filtered and washed with hot water and finally with ethanol to remove any contamination of ligand from the complex.

The precipitate was dried at 110-120° and weighed as $Pd(C_9H_8O_4N)_2$. It is insoluble in common organic solvents but soluble in pyridine, NaOH or NH_4OH solutions. Some of the results are given in Table 1. Conversion factor for Pd^{II} is 0.2152.

TABLE 1—DETERMINATION OF PALLADIUM(II)

Pd(II) taken mg	Weight of complex mg	Pd(II) found mg	Error mg
12.28	57.30	12.33	+05
6.14	28.60	6.15	+01
9.82	45.50	9.85	+03
18.42	85.8	18.46	+04

References

1. B. L. SHAH and C. M. DESAI, *South Gujarat Univ. J.*, 1981.
2. B. L. SHAH and C. M. DESAI, *Curr. Sci.*, submitted for publication.
3. A. I. VOGEL, "A Text Book of Practical Organic Chemistry", 3rd. ed., Longmans, London, 1955, p. 996.
4. D. N. SHAH and N. M. SHAH, *J. Indian Chem. Soc.*, 1949, 26, 235.

* South Gujrat University, Surat.

J. INDIAN CHEM. SOC., VOL. LXI, JULY 1984

Microgram Determination of Ascorbic Acid in Pharmaceutical Preparations, Urine, Blood Plasma and Fruit Juices

V. N. PATHAK, A. L. SINGH and I. C. SHUKLA

Department of Chemistry, University of Allahabad, Allahabad-211 002

Manuscript received 5 November 1982, revised 29 July 1983, accepted 30 May 1984

VARIOUS oxidants have been used for the titrimetric[1-10] and colorimetric[11-18] determination of ascorbic acid. Many of these methods suffer from the drawback of longer reaction time and lesser sensitivity. The standard method[11,14] used in pathological laboratories involves rigid control of temperature (37°), a reaction time of 3 hours and a complicated procedure. Moreover, the determination of ascorbic acid in urine is done titrimetrically[15] by a separate procedure. The present method utilises a quick reaction, gives better accuracy and more precise results. It is a simple and general procedure for the determination of ascorbic acid in its various forms and in biological fluids.

Experimental

Klett-Summerson photoelectric colorimeter was used for the absorbance measurement. Ammonium meta vanadata (A. R.) solution (0.3 *M*) 3.5 g (Reanal, Budapest), was made in 10% sulphuric acid (AnalaR, sp. gr., 1.84).

Preparation of samples: A fresh solution of pure ascorbic acid (tablets or injection ampule) was prepared in distilled water to give a concentration 1 mg ml^{-1}. 5 ml blood plasma was added dropwise with shaking to 5 ml trichloroacetic acid (20%) in a 25 ml centrifuge tube and stirred to obtain a fine suspension. The suspension was allowed to stand for 5 min and then centrifuged. The clear supernatant solution was filtered and used for the determination of ascorbic acid.

40 ml urine sample was taken and mixed well with 10 ml metaphosphoric acid (20%). The solution of urine was employed to estimate ascorbic acid.

Fruit juice of tomato, lemon and orange was mixed with 5 ml trichloroacetic acid (20%) to retard the oxidation of ascorbic acid and to precipitate protein etc. The solution was centrifuged and the supernatent layer was treated with 10 ml metaphosphoric acid (3%) and filtered. The filtrate was used for the determination of ascorbic acid.

Procedure: Aliquots containing 40 μg-0.8 mg ml^{-1} ascorbic acid were prepared by diluting the stock solution (1 mg ml^{-1}) with distilled water. The test solution (5 ml), standard ascorbic acid solution (5 ml, 200 μg ml^{-1}), and distilled water (5 ml) were taken in three separate stoppered corning test tubes. To each test tube ammonium meta vanadate reagent (5 ml) was added and the content were heated on a steam bath for 10 min. Reaction mixture was cooled to room temperature and the absorbance was measured at 680 nm or using red filter using reagent blank and the ascorbic acid content calculated.

Results and Discussion

The accuracy (established by recovery tests based on standard addition method) and the results of estimation of ascorbic acid in biological fluids are shown in Table 1 and compared with the standard method[14-18]. The characteristic green colour at 680 nm is due to complex formation between the oxidised state of ascorbic acid (dehydroascorbic acid) and tetravalent vanadium. It obeys Beer's law between 40μg-0.8mg ml^{-1} and the molar absorptivity for 1 μg ascorbic acid is 0.155. A green colour stable for several days, with a maximum deviation of $\pm 1\%$ was obtained within 10 min of heating on a steam bath. In the

TABLE 1—DETERMINATION OF ASCORBIC ACID WITH AMMONIUM META VANADATE REAGENT

A. Pure Sample

Concn. μg ml^{-1}	Mean recovery μg	Standard deviation	Coefficient variation %
40	40.32	0.06	0.15
200	200.00	0.25	0.13
400	400.00	0.48	0.12
680	680.65	0.57	0.09
800	800.00	0.65	0.08

B. Standard Addition Method

Formulation	Analysis % ; Present method	Standard method	Pure ascorbic acid Added mg	Found mg	Percentage recovery
Celin (250 mg)	99.1	99.0	24.0	23.9	99.5
Sorvicin (250 mg)	99.2	99.2	24.0	23.8	99.3
Redoxan (50 mg)	99.7	99.7	24.0	23.8	99.0

C. Biological Samples

Sample	Aliquot ml	Present Method (Ascorbic acid found*) μg	mg/100 ml	Standard Method μg	mg/100 ml
Blood	5	58	1.16	58.5	1.17
Plasma	5	112	2.24	112	2.24
Urine	2	204	10.2	205	10.25
	2	380	19.0	381	19.05
Tomato	0.5	515	103.0	515	103.0
Juice	0.5	422	84.4	421	84.2
Lemon	0.5	652	130.4	650	130.0
Juice	0.5	755	151.0	755	151.0
Orange	0.5	575	115.0	574	114.8
Juice	0.5	734	146.8	735	147.0

* Average of three concordant determinations.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 655-657

Mixed Complexes of Copper(II)

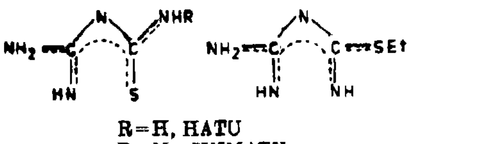
NITISH K. ROY* and CHITTA R. SAHA

Department of Chemistry, Indian Institute of Technology, Kharagpur-721 302

Manuscript received 3 October 1983, revised 23 March 1984, accepted 21 July 1984

The complexes of the type [CuLL″X] or [CuL′HL″]X$_2$ (LH = HATU, 1-amidino-2-thiourea or HNMATU, *N*-methyl-1-amidino-2-thiourea; L′H = HSEATU, *S*-ethyl-1-amidino-2-thiourea; L″ = α,α′-dipyridyl/*O*-phenanthroline; X = Cl/Br) have been isolated from methanol medium and characterized mainly from electronic spectra. The five coordinated complexes obtained for HATU and HNMATU contain square pyramidal geometry while HSEATU complexes contain square planar one.

FIVE coordinate copper(II) ion having square pyramidal or trigonal configuration have been reported in some mixed ligand complexes[1,2]. Copper(II) chelate containing a bidentate (NN) biguanide and α,α′-dipyridyl or *o*-phenanthroline (L″) have a pseudo-octahedral geometry with a CuN_4O_2 chromophore through participation of water molecules[3]. Tridentate (ONO) iminodiacetic acid and L″ also produce pseudo-octahedral copper(II) complexes with a coordinated water molecule[4]. However, copper(II) complexes with biguanide and picolinic acid are square planar[5]. 1-Amidino-2-thiourea (HATU) is quite similar to biguanide and is known to behave both as N, N and S, N donor to copper depending on experimental conditions[6,7]. It's *N*-methyl derivatives (HNMATU) and *S*-ethyl derivatives (HSEATU), however, behave only as S, N donor and N, N donor, respectively. The present paper reports the donor characteristics of these thioligands and the stereochemistry of copper(II) in its mixed ligand complexes.



R=H, HATU
R=Me, HNMATU

Experimental

Analytical grade reagents and pure distilled solvents were used throughout the work. Metal, halogen and sulphur were determined by classical methods and nitrogen was determined by semimicroanalytical technique. Vibrational and electronic spectral studies, magnetic and conductance measurements were carried out in Beckman IR-12 and Carry 17D, Guoy balance and Philips conductivity bridge, respectively.

Preparation of the complexes :

All the complexes were similarly prepared. The methanolic solution of LH or L′H (50 ml, 0.01 mol) was added[8] slowly to that of [CuL″X_2] (100 ml, 0.01 mol; X = Cl/Br) with continuous stirring at 0°. The solution was filtered and the filtrate kept in a desiccator for slow evaporation. Fine crystalline compounds obtained, were filtered and dried over fused $CaCl_2$.

Results and Discussion

The complexes are formulated from the analytical data (Table 1). It shows that the ligand HATU HNMATU behave as bidentated monoanion while HSEATU behaves as neutral bidentate. Molar conductance data (Table 1) also support the suggested formula. In the former cases, the conductance values are in the range 16-25 Ω^{-1} cm^2 mol^{-1} while in latter cases the values are 230-250 Ω^{-1} cm^2 mol^{-1} in the aqueous medium. The conductance value in former cases increases with time accompanied by change in colour from brown to green. These may be due to decomposition of the complexes. All the complexes are soluble in aqueous and many organic solvents. However, the solubility is more in the latter cases. The magnetic moment values are in the range 1.73-2.20 B.M. as expected for a single d-electron system.

The infrared spectral (Table 2) of three representative complexes are given for a few important bands. The bands due to N–C–S and C–S of the thioligands show a shift in the HATU (compound no. 3) and HNMATU (compound no. 6) complexes relative to the free ligands. In HSEATU complexes, no such change was observed. The bands at ~500 cm^{-1} (M–N) was observed only in all cases, but a new band at ~303 cm^{-1} was observed only in HATU and HNMATU complexes. These indicate the presence of SN bonding in these complexes unlike the HSEATU complexes. The appearence of three new peaks at ~1036, ~780 and ~772 cm^{-1} in the mixed complexes show the presence of bipyridyl or phenanthroline ring.

The electronic spectra of all these complexes in solid state and in solution are almost identical (Table 3). This indicates the non-participation of

* Chemical Laboratory (ER), Geological Survey of India, 27, Chowringee Road, Calcutta-700 016.

TABLE 1—ANALYTICAL, MAGNETIC AND MOLAR CONDUCTANCE DATA

Sl. no.	Compound	Colour	Analysis % ; Found/(Calcd.) M	N	S	halide	μ_e 300 K B.M.	Λ_M Ω^{-1} cm^2 mol^{-1}
1.	[Cu(ATU)(bipy)Cl]	Light brown	17.21 (17.07)	22.42 (22.59)	8.75 (8.60)	9.39 (9.54)	2.15	18^a
2.	[Cu(ATU)(bipy)Br]	Light brown	15.62 (15.48)	20.05 (20.16)	7.83 (7.64)	19.37 (19.28)	2.18	18^a
3.	[Cu(ATU)(phen)Cl]	Light brown	16.09 (16.03)	21.11 (21.21)	8.21 (8.08)	8.75 (8.96)	2.20	15^a
4.	[Cu(ATU)(phen)Br]	Light brown	14.52 (14.41)	19.01 (19.07)	7.40 (7.26)	18.32 (18.16)	2.18	15^a
5.	[Cu(NMATU)(bipy)Cl]	Light brown	16.38 (16.45)	21.67 (21.76)	8.37 (8.29)	9.28 (9.19)	2.01	20^a
6.	[Cu(NMATU)(bipy)Br]	Light brown	14.68 (14.75)	19.42 (19.51)	7.39 (7.43)	18.67 (18.58)	2.11	21^a
7.	[Cu(NMATU)(phen)Cl]	Light brown	15.42 (15.48)	20.42 (20.48)	7.82 (7.85)	8.72 (8.65)	2.08	23^a
8.	[Cu(NMATU)(phen)Br]	Light brown	13.80 (13.86)	18.40 (18.48)	7.50 (7.40)	17.69 (17.60)	2.11	22^a
9.	[Cu(SEATU)(bipy)]Cl_2	Greenish yellow	14.43 (14.58)	19.21 (19.31)	7.41 (7.35)	16.43 (16.32)	2.20	250^b
10.	[Cu(SEATU)(bipy)]Br_2	Greenish yellow	12.18 (12.11)	16.10 (16.03)	6.19 (6.10)	30.62 (30.53)	2.21	255^b
11.	[Cu(SEATU)(phen)]Cl_2	Greenish yellow	13.69 (13.80)	18.15 (18.26)	6.75 (6.66)	15.52 (15.43)	2.20	250^b
12.	[Cu(SEATU)(phen)]Br_2	Greenish yellow	11.51 (11.59)	15.25 (15.32)	5.22 (5.84)	29.30 (29.19)	2.20	250^b

a = In methanol, b = in water.

TABLE 2—INFRARED SPECTRAL BANDS (cm^{-1}) OF THE SELECTED COMPLEXES

Sl. no.	Compounds	dpy(1)	thio-ligand	dpy(2)	dpy(3)	C – S	M – N	M – S
1.	HATU		935			800		
2.	$Cu(ATU)_2$ (NN bonded)		930			815	480	
3.	[$Cu(ATU)_2$(bipy)Cl]	1036	890	780	772	715	510 490	335
4.	HNMATU		960			770		340
5.	[$Cu(NMATU)_2$]Cl_2		850			710	460	340
6.	[Cu(NMATU)(bipy)Cl	1032	870	775	770	725	490 470	330
7.	HSEATU Br					675		
8.	[$Cu(SEATU)_2$]Cl_2					670	485	
9.	[Cu(SEATU)(bipy)]Cl_2	1045		782	775	672	490 480	

solvent molecules in the coordination. The spectra of HATU and HNMATU complexes are very much different from those of CuL_2 complexes where only one band is observed (Table 3) in the visible region. The mixed complexes show broad peaks at ~ 13800 cm^{-1} (having a shoulder on the lower frequency side 13000 cm^{-1}) at ~ 18000 cm^{-1}, and a high intensity peak at ~ 23000 cm^{-1}. The low extinction coefficient values of the first two bands suggest d-d transition in an approximate D_{2h} symmetry. The ~ 23000 cm^{-1} band is most probably due to L→M transition. The bands at ~ 13800 cm^{-1} and ~ 18000 cm^{-1} may tentatively be assigned to d_{xy}, $d_{z^2} \rightarrow d_{x^2-y^2}$ and d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$, respectively. Similar type of spectra have been reported in a number of cases[9,10]. The geometry around copper for these complexes have been suggested to be square pyramidal. The shoulder at ~ 13000 cm^{-1} may be due to non-symmetrical environment around copper atom. The position of bands depend on halide ion indicating its involvement in the coordination. The peak positions of HNMATU complexes are at higher energy region with respect to HATU. This is expected as HNMATU is slightly a stronger ligand than HATU. The spectra of HSEATU complexes are similar to those of CuL'_2 complexes, and like CuL'_2, only one band is observed (Table 3). This indicates that there is no change in square planar geometry when one L' is replaced by L''.

From the above discussion it can be said that five coordinate complexes having square pyramidal geometry favour with the ligands HATU and HNMATU while complexes with HSEATU retain square planar geometry. In the former cases the bondings of the thio-ligands occur through both S, N donor atoms while with the latter through N, N donor atoms.

TABLE 3 — ELECTRONIC SPECTRAL BANDS (nm)* OF THE COMPLEXES

	Compound	Solvent	d_{xy}	$d_{z^2} \rightarrow d_{x^2+y^2}$	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$	Charge transfer
1.	[Cu(ATU)(bipy)Cl]	Solid	13,100 sh	13,760	18,780	24,090
		Methanol	13,070 sh	13,700 (45)	18,700 (105)	24,090
		DMF	13,070 sh	13,700 (47)	18,700 (107)	24,090
2.	[Cu(ATU)(bipy)Br]	Solid	13,250 sh	13,950	18,660	23,860
		Methanol	13,170 sh	13,900 (53)	18,600 (101)	22,800
		DMF	13,170 sh	13,900 (51)	18,600 (100)	23,800
3.	[Cu(ATU)(phen)Cl]	Solid	13,350 sh	14,100	18,850	24,380
		Methanol	13,250 sh	14,000 (59)	18,800 (107)	24,290
		DMF	13,260 sh	14,000 (51)	18,800 (101)	24,290
4.	[Cu(ATU)(phen)Br]	Solid	13,460 sh	14,250	18,950	24,200
		Methanol	13,370 sh	14,200 (49)	18,800 (104)	24,080
		DMF	13,350 sh	14,200 (55)	18,800 (107)	24,080
5.	[Cu(NMATU)(bipy)Cl]	Solid	13,210 sh	13,950	19,050	24,295
		Methanol	13,150 sh	13,910 (61)	18,990 (111)	24,290
		DMF	13,150 sh	13,910 (59)	18,900 (105)	24,295
6.	[Cu(NMATU)(bipy)Br]	Solid	13 090 sh	13,870	18,990	24,120
		Methanol	12,010 sh	13,850 (63)	18,950 (109)	24,120
		DMF	13,000 sh	13,830 (55)	18,950 (101)	24,120
7.	[Cu(NMATU)(phen)Cl]	Solid	13,350 sh	14,120	19,250	24,420
		Methanol	13,300 sh	14,070 (63)	19,130 (95)	24,420
		DMF		14,010 (51)	19,110 (100)	24,420
8.	[Cu(NMATU)(phen)Br]	Solid		14,030	19,120	24,290
		Methanol	13,150 sh	14,000 (60)	19,070 (105)	24,290
		DMF		13,980 (55)	19,090 (97)	24,290
9.	[Cu(SEATU)(bipy)]Cl_2	Methanol			19,250 (91)	29,510
		DMF			19,200 (89)	
10.	[Cu(SEATU)(bipy)]Cl_2	Methanol			19,250 (105)	29,470
		DMF			19,200 (101)	
11.	[Cu(SEATU)(phen)]Cl_2	Methanol			19,630 (97)	29,750
		DMF			19,570 (93)	
12.	[Cu(SEATU)(phen)]Br_2	Methanol			19,630 (91)	29,690
		DMF			19,570 (90)	
13.	$Cu(ATU)_2$(NN bonded)	Solid			18,460	28,020
14.	$[Cu(HNMATU)_2](ClO_4)_2$	Methanol			18,250 (120)	27,890
15.	$[Cu(HSEATU)_2]Cl_2$	Water			18,690 (101)	28,220

* ε values in parenthesis.

References

1. B. J. HATHAWAY and D. E. BILLING, *Coord. Chem. Rev.*, 1970, **5**, 143.
2. B. J. HATHAWAY and P. G. HODGSON, *J. Inorg. Nucl. Chem.*, 1973, **35**, 4071.
3. R. L. DUTTA, D. DE and A. SYAMAL, *J. Indian Chem. Soc.*, 1978, **45**, 664.
4. R. L. DUTTA, S. P. BANERJEE and D. DE, *J. Indian Chem. Soc.*, 1975, **52**, 582.
5. R. L. DUTTA and R. K. RAY, *J. Inorg. Nucl. Chem.*, 1979, **41**, 755.
6. C. R. SAHA and N. K. ROY, *J. Coord. Chem.*, 1983, **12**, 163.
7. N. K. ROY and C. R. SAHA, *Indian J. Chem., Sect. A*, 1980, **19**, 889.
8. R. E. WILDE, T. K. K. SRINIVASAN and S. N. GHOSH, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1017.
9. N. RAY, L. HULETT, R. SHEAHAN and B. HATHAWAY, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 305.
10. R. H. BALUNDGI and A. CHAKRAVORTY, *Inorg. Chem.*, 1973, **12**, 983.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 658-660

Nature of Addition Compounds of Naphthoxides of Titanium(IV) with Some Amides and Phosphoryl Ligands

K. C. MALHOTRA, K. C. MAHAJAN and S. C. CHAUDHRY

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla-171 005

Manuscript received 18 January 1984, revised 25 June 1984, accepted 21 July 1984

Di- and tri-chlorotitanium(IV)naphthoxides form compounds of composition $TiCl_2(OC_{10}H_7)_2.2L$ and $TiCl_3(OC_{10}H_7).2L$, while titanium tetranaphthoxide naphtholate forms compounds of composition $Ti(OC_{10}H_7)_4.L$, where L stands for phosphoryl and amide ligands. Based upon elemental analysis, conductance, molecular weight, T. G. A. and infrared spectral studies, their structures have been elucidated.

COMPARED to alkoxides[1] and phenoxides[2,3] little attention has been focussed on the chemistry of metal naphthoxides though they find applications as homogeneous catalysts in synthetic organic reactions[4,5]. In our earlier communication[6], we have reported the synthesis of naphthoxides of titanium(IV) and elucidated their structures. In continuation of these investigations, we now report the addition compounds of naphthoxides of titanium(IV) with some amides and phosphoryl ligands to establish their Lewis acid character.

Experimental

Titanium naphthoxides, $Ti(OC_{10}H_7)_4.C_{10}H_7OH$, $TiCl_3(OC_{10}H_7)$ and $TiCl_2(OC_{10}H_7)_2$ were prepared by the methods reported earlier[6]. All the chemicals used were AR grade and were purified by standard methods. Addition compounds of naphthoxides of titanium(IV) with various amides and phosphoryl ligands were prepared by reacting benzene solution or suspension of a known weight of parent titanium naphthoxide with the ligands under controlled experimental conditions because reactions were exothermic. The content were stirred for about 6 h, when the components went into solution and the compounds were isolated by the addition of petroleum ether. In some of the cases, the components were refluxed and the crystalline compounds separated out on cooling the resulting solutions. These were then filtered and dried under vacua.

Titanium was estimated as titanium dioxide and chlorine by Volhard's method. Molecular weights of the adducts were determined cryoscopically in nitrobenzene. Infrared spectra (KBr) were recorded using Perkin-Elmer 337 and 621 spectrophotometer. Thermal studies of the compounds were carried out on a Stanton Model AD−2 thermogravimetric balance.

Results and Discussion

Di- and tri-chlorotitanium(IV)naphthoxides form compounds of composition $TiCl_2(OC_{10}H_7)_2.2L$ and $TiCl_3(OC_{10}H_7).2L$ with *N*-methylformamide, *N,N'*-dimethylformamide, *N*-methylacetamide, *N,N'*-dimethylacetamide, dimethylsulphoxide, hexamethylformamide and triphenylphosphine oxide, while titanium tetranaphthoxide naphtholate forms compounds of composition $Ti(OC_{10}H_7)_4.L$ with these ligands. Stoichiometric composition of these compounds has been established by elemental analysis (Table 1). The compounds are moisture sensitive but stable in dry atmosphere. Molar conductances using millimolar solutions of most of these compounds in nitrobenzene are very low compared to the values of 1 : 1 electrolytes, thus indicating their predominantly non-ionic nature. Molecular weights of some of these compounds, where solubility permitted in nitrobenzene suggest that the compounds of composition $TiCl_3(OC_{10}H_7).2L$ and $TiCl_2(OC_{10}H_7)_2.2L$ are monomers whereas those of the composition $Ti(OC_{10}H_7)_4.L$ are dimers.

Significant ir bands (ν_{max}) of these adducts are due to NH, C=O, C−N and N−C=O in case of amides and P=O, P−N and P−C in case of phosphoryl ligands (Table 1). The $\nu_{C=O}$ of the free amides occuring at 1685, 1670, 1680 and 1670 cm^{-1} for NMF, NMA, DMF and DMA gets lowered by ~ 40-50 cm^{-1} on complexation suggesting coordination through the oxygen atom of the carbonyl group which is further supported by a trend in shifts of ν_{NH}, ν_{C-N} and $\nu_{N-C=O}$ vibrational modes towards higher regions[7-9]. In the case of dimethylsulphoxide adducts, the band present at 1050 cm^{-1} (S=O) in the pure ligand is lowered by ~70-80 cm^{-1}, while the band at 690 cm^{-1} (C−S) shifts to higher regions which supports oxygen coordination and is in agreement with the earlier reports[10]. Similarly, $\nu_{P=O}$ of triphenylphosphine oxide[11,12] and hexamethylphosphoramide[13] observed at 1192 and 1210 cm^{-1}, respectively is lowered by ~50-60 cm^{-1} on adduct formation due to polarisation of the oxo-bond by the acceptor atom[14]. Other characteristic vibrations of hexamethylphosphoramide and triphenylphosphine oxide which are perturbed are due to ν_{P-N} and ν_{P-C} stretching modes. The two bands at 984 and 740

TABLE 1—ANALYTICAL AND SPECTRAL (cm^{-1}) DATA OF THE ADDUCTS OF NAPHTHOXIDES OF TITANIUM(IV) WITH AMIDES AND PHOSPHORYL LIGANDS

Compound	Colour	M.p. °C	Analysis% Found/(Calcd.) Ti	Cl	Molar conductance in $PhNO_2$ ohm^{-1} cm^2 mol^{-1}	Mol. Wt. Found/ (Calcd.)	ν_{max} (cm^{-1}) C=O or P=O	C–N or P–N	N–C=O or P–C	Ti–O	Ti–Cl
A.2NMF	Brown	109	11.43 (11.55)	25.50 (25.63)	2.1	—	1638	1400 3290[c]	765	608	352,348
A.2DMF	Dark brown	67	10.74 (10.82)	23.89 (24.01)	2.6	401 (443.5)	1635	1470	678	605	348,341
A.2NMA	Brown	85	10.79 (10.82)	23.90 (24.01)	3.0	—	1628	1300 3280[c]	767	596	349,340
A.2DMA	Brown	105	10.00 (10.18)	22.41 (22.59)	4 1	410 (458.5)	1628	1524	735	595	341,338
A.2DMSO	Brown	91	10.47 (10.58)	23.36 (23.48)	3.3	489 (528)	960[a]	730[b]	—	599	351,346
B.2NMF	Light brown	88	9.02 (9.18)	13.51 (13.58)	2.0	—	1645	1419 3352[c]	760	598	349
B.2DMF	Brown	64	8.58 (8.71)	12.73 (12.89)	2.1	—	1642	1475	665	592	342
B.2NMA	Brown	90	8.68 (8.71)	12.80 (12.89)	3.1	514 (551)	1638	1324 3342[c]	763	608	346
B.2DMA	Brown	55	8.17 (8.29)	12.09 (12.26)	1.9	549 (579)	1640	1528	740	602	348
B.2DMSO	Brown	71	8.40 (8.56)	12.57 (12.66)	2.6	527 (561)	975[a]	720[b]	—	602	305
C.NMF	Light brown	179	7.00 (7.07)	—	1.0	1319 (679)	1648	1416 3355[c]	758	602 598 508	—
C.DMF	Light brown	183	6.83 (6.93)	—	1.3	—	1646	1465	680	600 595 518	—
C.NMA	Brown	170	6.79 (6.93)	—	1.6	—	1640	1318 3345[c]	758	601 592 510	—
C.DMA	Light brown	202	6.71 (6.79)	—	1.0	—	1642	1529	730	608 601 508	—
C.DMSO	Brown	196	6.77 (6.88)	—	1.1	—	900[a]	730[b]	—	602 598 512	
A.2HMPA	Brownish red	110	7.27 (7.32)	16.07 (16.25)	4.1	605 (655)	1148	1056 994 750	—	602	351,348
A.2Ph_3PO	Red	72	5.57 (5.62)	12.33 (12.48)	3.4	—	1135	—	465 451	598	348,350
B.2HMPA	Brown	93	6.21 (6 29)	9.17 (9.31)	2 7	—	1158	1062 997 755	—	608	346
B.2Ph_3PO	Dull red	107	4.90 (4.99)	7.21 (7.39)	3.0	932 (961)	1145	—	474 458	604	350
C.HMPA	Light brown	179	5.79 (6.01)	—	1.0	1557 (799)	1162	1060 996 758	—	610 507	—
C.Ph_3PO	Light red	94	5.21 (5.35)	—	1.7	—	1148	—	476 460	606 505	—

A = $TiCl_3(OC_{10}H_7)$, B = $TiCl_2(OC_{10}H_7)_2$, C = $Ti(OC_{10}H_7)_4$.
a = ν(S=O), b = ν(C–S), c = ν(N–H).

cm^{-1} (P–N) in parent HMPA shift to higher regions in its adducts possibly due to the increase in delocalisation of nitrogen electron pair towards the phosphorus atom[14]. The bands at 455 and 441 cm^{-1} (P–C) in case of pure Ph_3PO also move towards higher frequencies by ~10-15 cm^{-1} which agrees well with the earlier reports on such adducts. All these bands are given in Table 1.

Other important absorptions observed in the ir spectra are due to titanium-oxygen and titanium-chlorine stretching modes. The bands at 508-512 cm^{-1} due to bridging $Ti\diagup^{O}\searrow Ti$ modes in the parent naphthoxides[6] are absent in the compounds $TiCl_3(OC_{10}H_7)$.2L and $TiCl_2(OC_{10}H_7)_2$.2L suggesting the rupturing of naphthoxy-bridges on complexation with the ligands. These observations are in agreement with the earlier reports on the alkoxide and phenoxide adducts with various bases[15,16]. Sharp bands in the region 590-610 cm^{-1} may be assigned to terminal ν_{Ti-O} stretching modes[6,9]. The appearance of bands in the region 340-350 cm^{-1} (Ti–Cl) of the adducts suggest an octahedral environment around titanium[9,17]. However, the adducts of titanium tetranaphthoxide naphtholate of composition $Ti(OC_{10}H_7)_4$.L exhibit bands due to both

terminal Ti – O as well as bridging Ti–O→Ti modes which suggest that in these compounds the bridging is retained even on adduct formation.

Thermogravimetric analysis of some of the adducts has been studied to determine their stability and mode of decomposition. From the weight changes noted in the thermograms of different compounds, it is inferred that the first step of decomposition involves the loss of base molecule at 170-22[illegible] followed by a similar trend of decomposition as observed for the parent naphthoxides[6].

References

1. D. C. Bradley, *Prog. Inorg. Chem.*, 1960, **2**, 303; *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259.
2. K. C. Malhotra and R. L. Martin, *J. Organomet. Chem.*, 1982, **239**, 159.
3. V. R. Masthoff, H. Kohler, H. Bohland and F. Schmeil, *Z. Chem.*, 1965, **5**, 122.
4. S. M. Ohlberg and P. A. Vandermaulen, *J. Am. Chem. Soc.*, 1953, **75**, 997.
5. C. Konehny, *Collect. Czech. Chem. Commun.*, 1962, **27**, 2596.
6. K. C. Malhotra, K. C. Mahajan and S. C. Chaudhry, *J. Indian Chem. Soc.*, 1983, **60**, 636.
7. R. C. Paul, H. Madan and S. L. Chadha, *J. Inorg. Nucl. Chem.*, 1974, **36**, 737; 1975, **37**, 447.
8. R. C. Paul, H. S. Makhni, P. Singh and S. L. Chadha, *J. Less-Common Met.*, 1969, **17**, 437.
9. K. C. Malhotra, N. Sharma and S. C. Chaudhry, *Transition Met. Chem.*, 1981, **6**, 238.
10. M. F. Lappert and J. K. Smith, *J. Chem. Soc.*, 1961, 3224.
11. K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, 1963, **17**, 1875.
12. J. P. Clark, V. M. Langford and C. J. Wilkins, *J. Chem. Soc.*, 1967, 792.
13. J. A. Sylvanovich, Jr. and S. K. Madan, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1675.
14. M. W. G. de Bolster, "The Coordination Chemistry of Aminophosphine Oxides and Related Compounds", Preprinted Thesis, Leiden, 1972.
15. K. C. Malhotra, U. K. Banerjee and S. C. Chaudhry, *Transition Met. Chem.*, 1982, **7**, 14.
16. K. Behzadi and A. Thompson, *J. Less-Common Met.*, 1970, **9**, 56.
17. R. C. Paul, P. Gupta and S. L. Chadha, *J. Inorg. Nucl. Chem.*, 1977, **13**, 665.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 661-663

Corrosion Behaviour of Lead in Chloroacetic Acid Solutions

E. A. HASSAN, F. H. KAMAL, A. R. EBAID and M. Y. MOURAD

Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt

Manuscript received 7 June 1982, accepted 3 August 1983

The corrosion behaviour of lead in aqueous solutions of mono-, di-, and tri-chloroacetic acids at different concentrations has been investigated. The maximum steady state potentials are achieved from the diagrams of potential-time measurements. The shift of steady state potential towards more negative values with increasing acid concentration is probably due to less formation of insoluble corrosion products which adhere to the metal surface. The obtained potential values are found to be related to the concentration of the acid solution by the equation E = a − b log c. The corrosion rate dw/dt per unit projected area of specimen, increases with the concentration of bulk solution. It is suggested that the corrosion of lead in the three acids is anodically controlled. The values of critical current density for passivation are found to depend on the acid concentration in solution and on the nature of the anion studied.

EARLIER work has adequately demonstrated that protective coatings are formed on lead in acetic acid solutions[1]. The corrosion of Pb in fatty acids can proceed only according to the reactions[2]

$$Pb + 2R-COOH \longrightarrow (R-COO)_2Pb + 2H$$
$$2H + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

The existence of monovalent lead ions in aqueous solutions was first reported by Denham and Allmand[3]. In a later study[4] of the anodic dissolution of lead it was suggested that in some solutions, lead dissolved as monovalent ions and the dissolution to be occuring by two simultaneous processes.

$$Pb(s) \longrightarrow Pb^{+}(aq) + e$$
$$Pb(s) \longrightarrow Pb^{++}(aq) + 2e$$

The present work deals with the corrosion behaviour of lead in stagnant solutions of mono-, di-, and tri-chloroacetic acid. Steady state potentials have been studied as a function of both time and acid concentration. The corrosion rate of lead metal has been further determined using the weight-loss procedure.

Experimental

The lead electrodes used were made from electrolytic lead sticks (BDH) in the form of short rods (0.9 cm dia. × 2.2 cm) fixed to pyrex glass tubes by araldite. Electrical contacts were achieved through thick copper wires soldered to one end of the rods. The electrodes were abraded successively with 1.0 and 0.0 grades emery papers and then degreased with acetone. The electrode vessel (60 ml) was made of pyrex glass without any rubber connections. The potential of lead electrodes was measured in solutions of AR grade mono-, di-, and tri-chloroacetic acids (10^{-3}-5×10^{-1} *M*). Potentials were measured, against SCE using a Pye potentiometer in conjunction with Scalamp galvanometer type MSZ-808. Steady state potentials were considered as when the potential did not alter by more than 1 mV/5 min. Each experiment was carried out with a newly polished electrode and with a fresh portion of the solution at 24-26°.

Weight-loss experiments were carried out using lead specimens (5 cm × 2 cm × 1 mm). These were abraded, degreased, washed, dried and weighed, followed by immersion in 100 ml the test solution at the required temperature. The type and extent of attack were determined at different time periods and at the end of the test period. The samples were then cleaned by water, dried and finally weighed. Solution loss by evaporation was compensated by the addition of double-distilled water. The dissolved lead ions were determined volumetrically using reported method[5].

The study of critical current density of passivation (I crit.) and its dependence on acid concentration was carried out using galvanostatic procedure[6].

Results and Discussion

Potential-time measurements : Potential-time curves for lead electrodes in stagnant solutions of mono-, di-, and tri-chloroacetic acids, under open circuit conditions, show that the steady state potential values are shifted towards the negative direction with increasing concentrations, 10^{-3} to 5×10^{-1} *M*. This behaviours is similar to that cited for cadmium electrodes in aqueous solutions of mono-, and tri-chloroacetic acids[7] and the corrosion properties of the aggressive ions[8,9]. However, it is found[10] that the maximum steady state potentials are achieved from positive direction, in case of copper electrodes in similar acid solutions.

Results of the effect of the molar concentration (c) of the three acids on the values of steady state potential of lead electrodes (Fig. 1), show that the straight line portions of these curves obey a relationship of type (1).

$$E = a - b \log c \qquad (1)$$

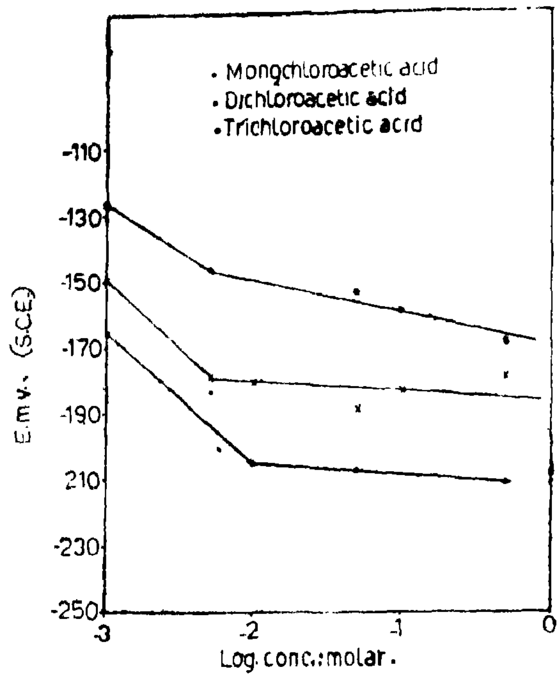


Fig. 1. E. mv. vs log for lead in mono-, di-, and tri-chloroacetic acid solutions.

where a and b are constants depending on the nature of electrolyte, and surface preparation[8,11]. The values of b range from 5 to 8 mV in concentration 5×10^{-1}-10^{-2} *M* and approximately equal to 30 mV in more dilute solutions. For one and the same acid the potential becomes more negative as the acid concentration increases (Fig. 1).

The shift of the steady state potential values of lead electrode towards less negative values proceeds according to the order, mono- > di- > tri-chloroacetic acid. This behaviour may be explained on the basis of the probable formation of insoluble corrosion products which adhere to the metal surface.

Weight-loss experiments : Results of immersion tests for 5 h in 10^{-3}-5×10^{-1} *M* acid solutions showed that the weight loss increases linearly with time. The corrosion rates, computed from the linear plots of weight-loss *vs* time are presented in Table 1.

TABLE 1—VARIATION OF CORROSION RATE WITH THE CONCENTRATION OF CHLOROACETIC ACID SOLUTIONS

Acid concn. *M*	Corrosion rate, mg/cm²/h Mono-	Di-	Tri-
5×10^{-1}	0.20	3.75	4.00
10^{-1}	0.14	1.90	3.40
5×10^{-2}	0.12	0.35	2.60
10^{-2}	0 10	0.30	0.40
10^{-3}	0.05	0.05	0.07

The corrosion rate was found to be related to the molar concentration of the acid by equation (2).

$$dw/dt = Kc^n \qquad (2)$$

where, c is the molar concentration and K and n are constants depending on the surface preparation of the metal and type of solution[8].

Plots of log corrosion rate *vs* log molar concentration of the acid solutions give striaght lines with slopes ranging between 0.3-0.8 mg/cm²/h (Fig. 2). The positive slopes indicate that the rate of corrosion of lead increases with the acid concentration. The increase in corrosion rate on going from mono-, di-, to tri-chloroacetic acid solutions is attributed to the increase of aggressiveness of these acids. The increase in corrosion rate, as well as the negative shift in the steady state potential values, with increasing acid concentration, may lead to the suggestion that the corrosion process is determined by depolarization of the anodic controlling reaction, *i.e.* the corrosion process is anodically controlled[13-14].

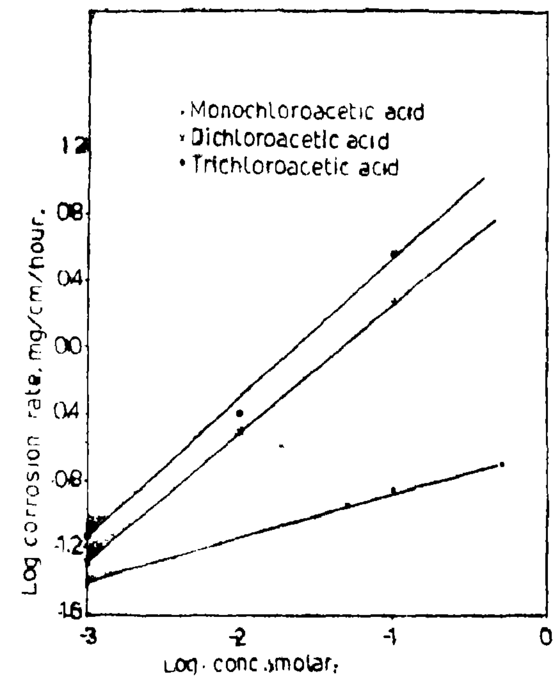


Fig. 2. Relation between corrosion rate of lead and concentration of mono-, di-, and tri-chloroacetic acid solutions.

Further insight into the role of anions (mono-, di-, and tri-chloroacetate) in relation to the corrosion behaviour of lead in stagnant solutions could be gained from the dependence of the critical current densities for passivation (I crit.) on concentration. (I crit.) was taken as a measure of the effectiveness of electrolyte used as inhibitor or corrosive[15]. Thus when lead is anodically polarized in different solutions, the magnitude of (I crit.) indicates the activation or passivation characters of the anions. Results given in Fig. 3 for the relationship between log c and log (I crit.), show that the latter can be expressed by the following form (3).

$$\log (\text{I crit.}) = a' + b' \log (c) \qquad (3)$$

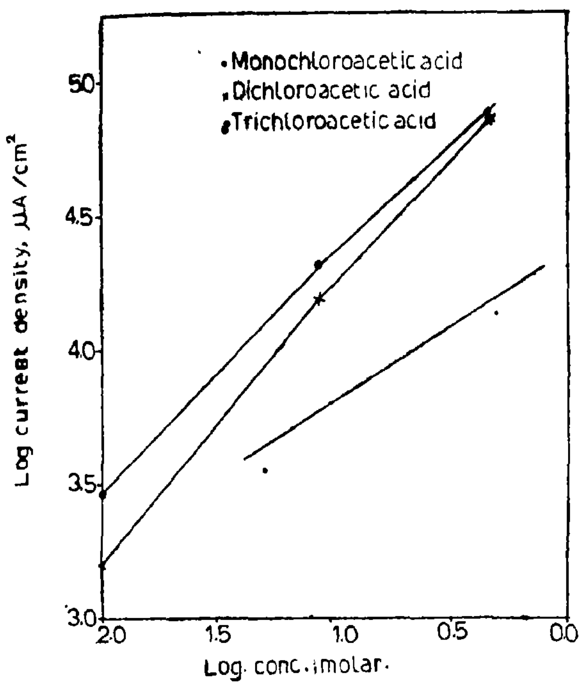


Fig. 3. Relation between current density and concentration of mono-, di-, and tri-chloroacetic acid solutions

where the constant a′ depends on the anionic nature and the value of b′ = 0.6, 0.9 and 1.02 for the three acids, respectively. The values of the critical current density proceed according to the following order :

Mono- < Di- < Tri-chloroacetic acid.

References

1. E. Laengle, *Schweiz. Arch. Angew. Wiss. Tech.*, 1968, **34**, 109, 147 (*Chem. Abstr.*, 1968, **69**, 89825).
2. T. A. Miskinova and L. G. Gindin, *Zashchita Metal*, 1965, **1**, 195 (*Chem. Abstr.*, 1965, **63**, 5342).
3. H. G. Denham and A. J. Allmand, *J. Chem. Soc.*, 1908, **93**, 424.
4. N. M. Bell, *Trans. Faraday Soc.*, 1915, **11**, 79.
5. G. Schwarzenbach, "Complexometric Titrations," Muthuen, London, 1954.
6. H. H. Uhlig and G. E. Woodside, *J. Phys. Chem.*, 1958, **57**, 280.
7. L. A. Kamel, V. Gouda, E. A. Hassan and F. M. Hafiz, *Indian J. Chem., Sect. A*, 1979, **17**, 242.
8. D. M. Brasher, *Nature (London)*, 1962, **193**, 868.
9. V. K. Gouda, M. G. A. Kheder and A. M. Shams El-Din, *Corrosion Sci.*, 1967, **7**, 221.
10. E. A. Hassan, S. M. Abdel Wahaab and M. M. Hegazi, *Indian J. Chem., Sect. A*, 1979, **17**, 567.
11. D. M. Brasher, J. Ch. Beryron, A. D. Mercex and J. E. R. Brouin, C. R. Lemo Symp. Eur. Inhibit. Corr., Ferrara, Italy, 1965, pp. 22, 559.
12. U. R. Evans, "Metallic Corrosion, Passivity and Protection", Edward Arnold, London, 1941.
13. A. Goswami, *J. Sci. Ind. Res., Sect. B*, 1956, **15**, 340.
14. N. D. Tomoshov, "Theory of Corrosion and Protection of Metals", Macmillan Co., New York, 1966, pp. 332, 408, 684.
15. E. F Duferk and D. S. McKinney, *J. Electrochem. Soc.*, 1956, **103**, 645.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 664-666

Effect of Halide Additives on the Corrosion Behaviour of Lead in Chloroacetic Acid Solutions

E. A. HASSAN, A. S. ABO EL-MAGD, F. H. KAMAL, A. R. EBAID and M. Y. MOURAD

Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt

Manuscript received 7 June 1982, accepted 3 August 1983

The effect of Cl^-, Br^- and I^- ions on the corrosion behaviour of lead electrodes in aqueous solutions of mono-, di- and tri-chloroacetic acids is evaluated by studying the potential-time and weight-loss measurements. It has been found that the steady-state potentials which obey the relationship E = a − b log c, are shifted towards more negative values with the increase in the concentration of the additive ions.

The decrease in the rate of corrosion with the increase of anion concentration, is probably due to the halide ions acting as anodic inhibitors.

SOME anions promote corrosion while others act as inhibitors. The decision between one or the other behaviour is said to depend on the solubility of the reaction products[1], adsorption[2], ion size and charge[3], ion deformability[4] and the electrostatic field set up by the negative charge of the anion on adsorption sites[5]. Generally, all anions present in large dilutions are corrosive[6], but tend to inhibit it in relatively concentrated solutions.

The effect of Cl^- as additive on the cathodic deposition of metals on Hg was investigated[7]. The observed effect of halide ions in decreasing the activation energy was attributed to the formation on the electrode of an intermediate complex ($Cl-M^{n+}$), in which the Cl^- acts as an electronic bridge. The retardation of the reaction between HNO_3 and Sn, by iodides of Na and K, is explained[8] to be due to the specific action of the alkali ions. The inhibition action of NaI, KI and LiI to the reaction accompanied by the formation of thin layer of stannous iodide on the surface of tin, is attributed to the formation of the oxidation products of HI in the reaction mixture.

In the present work, the effect of Cl^-, Br^- and I^- on the corrosion behaviour of lead, is studied in aqueous solutions of mono-, di-, and tri-chloroacetic acids. Steady state potential as a function of both time and concentration of acid containing different anions has been studied. The corrosion rate of lead metal has also been evaluated using the weight-loss procedure.

Experimental

The established steady state potentials of pure lead electrodes were measured in solutions of potassium salts of Cl, Br and I at varying concentrations (10^{-3}-$10^{-1}M$) in 0.1*M* mono-, di-, and tri-chloroacetic acid solutions.

The lead electrodes used, their preparation and treatment, electrode vessel, procedure and apparatus for measurements, and the weight-loss technique were the same as reported previously[6].

Results and Discussion

Potential-time measurements : Potential time curves for lead electrodes in 0.1*M* mono-, di-, and tri-chloroacetic acid solutions containing Cl^-, Br^- and I^- at concentrations of 10^{-3} to 10^{-1} *M* carried out under open circuit conditions, showed that the steady-state potential values are shifted towards a more negative direction with increasing additive concentration. Such behaviour may be due to the adsorption of halide anions on the metal surface[10].

The negative shift in the values of steady-state potential in presence of Cl^-, Br^- and I^- is higher as compared to the effect of changing the respective concentration of chloroacetic acid solutions, free from halide ions.

Results given in Fig. 1 show the relationship between the molar concentration (c) of halide ion added to 0.1 *M* solution of the three acids and the values of steady-state potential of lead electrodes. In all cases, the potential decreases with increasing the halide ion concentration. The straight line relationships are found to obey a relation of the type (1).

$$E = a - b \log c \qquad (1)$$

where a and b are constants depending on the nature of electrolyte and surface preparation[6,11].

The slopes obtained from the linear plots (b values) given in Table 1, show similar relationships as found for steel[12] and zinc[13] in neutral salt solutions, and cadmium in acid solutions. The decrease in the b values seems to be related to the decrease in aggressiveness of the anion.

Weight-loss measurements : The study of weight-loss measurements in 0.1 *M* solutions of mono-,

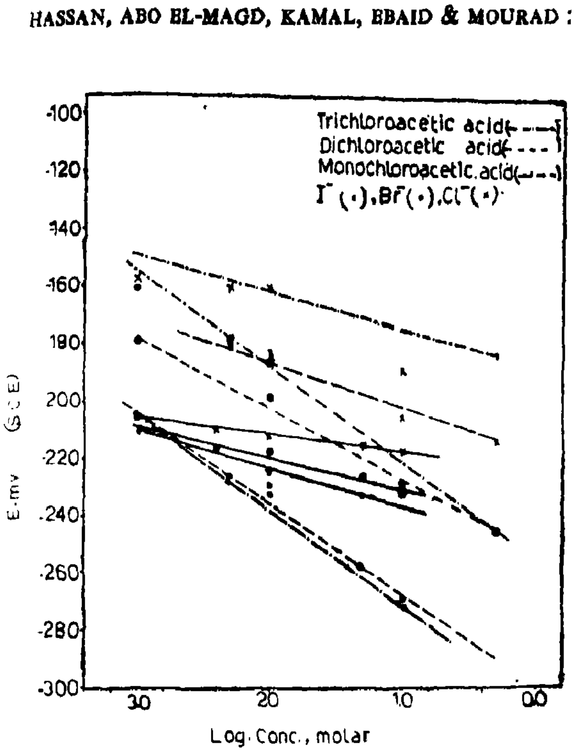


Fig. 1. E. mv. *vs* log c for lead in mono-, di-, and tri-chloroacetic acids in presence of iodide bromide and chloride.

TABLE 1—VALUES OF b OBTAINED IN 0.1 *M* SOLUTION OF MONO-, DI-, AND TRI-CHLOROACETIC ACIDS IN PRESENCE OF Cl^-, Br^- AND I^-

Chloroacetic acid	Values of b in presence of		
	Cl^-	Br^-	I^-
Mono-	−5.2	−10.2	−13.2
Di-	−14.0	−24.0	−24.0
Tri-	−16.0	−30.0	−33.5

are constants depending on the surface preparation of the metal and the nature of solution[9,11]. The plots of log corrosion rate *vs* log molar concentration of the acid solutions containing halide ions give straight lines with slopes (b) of 0.275, 0.400 and 0.650 for Cl^-, 0.220, 0.250 and 0.425 for Br^-, and 0.210, 0.115 and 0.125 for I^- in mono-, di-, and tri-chloroacetic acid solutions, respectively (Fig. 2).

The decrease in corrosion rate with the increase of anion concentration suggests that the halide ions act as anodic inhibitors. The inhibitive function of these ions may be associated with their ability to become adsorbed on the metal surface retarding the entry of Pb^{II} ions into the solution at the

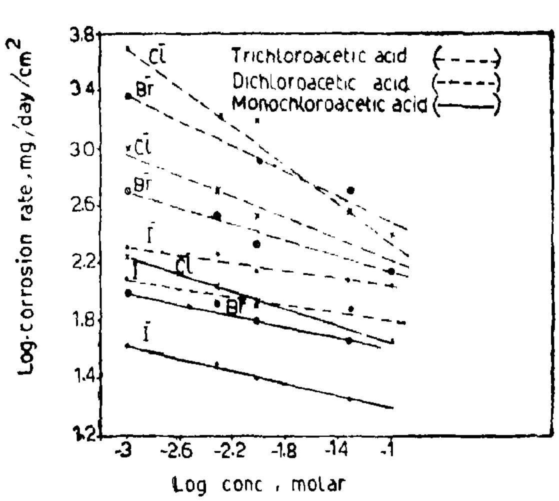


Fig. 2. Effect of anion concentration on corrosion rate for lead in 0.1 *M* solution of mono-, di-, and tri-chloroacetic acids containing halide ions.

TABLE 2—VARIATION OF CORROSION RATE WITH ANION (HALIDE) CONCENTRATIONS IN SOLUTIONS OF DIFFERENT CHLOROACETIC ACID

Anion conc. $\times 10^3$ *M*	Corrosion rate, $\times 10^{-3}$ mg/day/cm²								
	Cl^-			Br^-			I^-		
	Mono-	Di-	Tri-	Mono-	Di-	Tri-	Mono-	Di-	Tri-
1	1.75	9.94	48.0	0.96	4.80	22.2	0.42	1.20	1.95
5	1.10	5.04	16.8	0.82	3.36	13.8	0.31	0.83	1.77
10	0.91	3.74	15.6	0.62	2.10	7.8	0.25	0.82	1.32
50	—	—	3.6	0.46	—	4.8	—	0.78	1.26
100	0.48	2.50	0.9	0.53	1.44	1.8	0.16	—	1.12

di-, and tri-chloroacetic acids, in presence of Cl^-, Br^- and I^- within concentration range 10^{-3}-$10^{-1}M$, showed that the weight-loss increases linearly with time. The values of corrosion rate calculated from the straight lines, are presented in Table 2. The relationship between the corrosion rate and molar concentration of the acids containing halide ions follows the equation (2).

$$dw/dt = ac^{-b} \qquad (2)$$

where dw/dt is the corrosion rate in mg day^{-1} dm^{-2} ; c is the molar concentration, and a and b

anodes. The fact that the double logarithm relation between corrosion rate and salt concentration covers 3-4 orders of magnitude may suggest that the corrosion of lead in halide solutions is controlled by adsorption of anions on the active sites[15].

References

1. U. R. EVANS, "The Corrosion and Oxidation of Metals", Arnold, London, 1960, p. 139.
2. C. P. DE, *Nature* (*London*), 1958, **181**, 1060.
3. M. J. PRYOR, *Z. Electrochem.*, 1958, **62**, 782.

4. R. PIONTELLI, *Z. Electrochem.*, 1951, **55**, 128.
5. G. H. CARTLEDGE, *J. Phys. Chem.*, 1952, **60**, 32.
6. D. M. BRASHER, *Nature* (*London*), 1962 **193**, 868.
7. M. A. LOSHKAREV, A. A. KRUYKOVA, Y. M. LOSHKAREV and T. F. DYACHENKO, *Electrochem. Acta*, 1964, **9**, 1119.
8. G. S. KASBEKAR and A. R. NORMAMD, *Proc. Indian Acad. Sci., Sect. A*, 1939, **10**, 37.
9. E. A. HASSAN, F. H. KAMAL, A. R. EBAID and M. Y. MOURAD, *J. Indian Chem. Soc.*, 1984, **61**, 661.
10. YA. M. KOLOTYRKIN, *Chem. Abstr.*, 1960, **54**, 8247.
11. D. M. BRASHER, J. CR. BERYRON, A. D. MERCER and J. E. R. BROUIN, C. R. Lemo Symp. Enr. Inhibit. Corr., Ferrara, Italy, pp. 22, 559.
12. D. M. BRASHER, *Br. Corros. J.*, 1967, **2**, 95.
13. V. K. GOUDA, M. G. A. KHEDR and A. M. SHAMS EL-DIN, *Corrosion Sci.*, 1967, **7**, 221.
14. L. A. KAMEL, V. GOUDA, E. A. HASSAN and F. M HAFIZ, *Indian J. Chem., Sect. A*, 1979, **17**, 242.
15. A. A. ABDUL AZIM, K. VENICE GOUDA, A. LAILA SHALABY and E. SAFA AFIFI, *Br. Corros. J.*, 1973, **8**, 76.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 667-669

Intermediate Phases in Binary Liquid Crystalline Systems

N. K. SHARMA* and R. K. BAMEZAI

Department of Chemistry, University of Jammu, Jammu (Tawi)-180 001

Manuscript received 29 March 1983, accepted 21 July 1984

The diagrams of state of three binary systems have been studied. One of these shows appearance of intermediate phases of the type N and S_A, while in the other two diagrams, either N or S_A phase, as intermediate one, are observed. The explanation for their appearance is provided. The smectic C and smectic I phases of HOAB remain restricted on its respective side and do not show any miscibility with smectic C phases of HBBA and HBOA.

THE occurrence of electron donor acceptor (EDA) interactions in liquid crystals was provided in homologous series of 4,4'-bis-[n-alkyl-amino]-biphenyls[1]. Induced nematic and smectic phases were found in mixtures of potentially liquid crystalline donors and acceptors[2]. The charge transfer bands in the visible region have been observed in some liquid crystalline mixed phases[3]. The formation of induced smectic phases is said to occur whenever there is an enhancement in the liquid crystalline-isotropic transition temperatures[4]. Further, in some cases, a change in colour in the region of mixed phases in contact preparations[3] was observed. In case of intermediate phases, neither the enhancement in the liquid crystalline-isotropic transition temperatures nor any charge transfer interaction was observed. This paper reports the diagrams of state between HOAB as one component, and BBEA, HBBA and HBOA as the other ones, in which the intermediate phases have been observed.

Experimental

Materials: The following substances, with their known polymorphy were used in this work.

(i) 4,4'-Bis-n-hexadecyloxy-azoxybenzene (HOAB); $C_{16}H_{33}O-C_6H_4-N=N(\rightarrow O)-C_6H_4-OC_{16}H_{33}$ (Found Cr†. 89.2 S_I 91.4 S_C 115.7 Is. Requires[5] Cr. 89.5 S_B 91.1 S_C 115.5 Is).

The low temperature smectic phase, which was earlier classified as S_B, has now been classified as smectic I phase. This classification depends on the textural and the miscibility studies[6].

(ii) *N*-[4-n-Butyloxy-benzylidene]-4'-ethylaniline (BBEA); $C_4H_9O-C_6H_4-CH=N-C_6H_4-C_2H_5$ (Found Cr. 37.8 S_G 50.0 N 65.0 Is. Requires Cr. 38.7 S_G 50.5 N 64.8 Is).

(iii) *N*-[4-*n*-Heptyloxy-benzylidene]-4'-n-butyla line (HBBA); $C_7H_{15}O-C_6H_4-CH=N-C_6H_4$ C_4H_9 (Found Cr. 32.6 S_G 63.2 S_C 65.0 S_A 74.2 76.7 Is. Requires Cr. 31.5 S_G 62.5 S_C 63.6 S_A 73.0 75.5 Is).

(iv) *N*-[4-n-Heptyloxy-benzylidene]-4'-n-octyla line (HBOA); $C_7H_{15}O-C_6H_4-CH=N-C_6H_4$ C_8H_{17} (Found Cr. 48.0 S_G 52.7 S_B 68.7 S_C 7 S_A 83.0 Is. Requires Cr. 48.0 S_G 52.5-53.0 S_B 68 69.0 S_C 70.3 S_A 82.7-83.0 Is).

The transition temperatures and classification the phases BBEA, HBBA and HBOA are the sa as assigned in the earlier reports[7,8], except for t low temperature phase represented as smectic which has now been agreed to be represented smectic G phase[9].

Microscopic study: The miscibility investi tions on HOAB as one component, and BBE HBBA or HBOA as the other one were carried o on a polarizing microscope fitted with a microhe ing stage by Koffler's contact method[10].

Results and Discussion

The binary systems were so chosen that o liquid crystal shows low temperature smect I modification (HOAB), and the other possess smectic B or smectic G or both the phases (BBE HBBA, HBOA). The results of different bina systems are as follows.

System 1 (HOAB/BBEA): The diagram state of this binary system is provided in Fig. S_C and S_I modifications of HOAB and N and phases of BBEA remain restricted to their respecti sides. S_A and N appear as intermediate phase S_A phase appears at 97.5° from isotropic liquid a solidifies by 81.3°. Similarly, nematic phase appea at 91.3° on cooling the preparation and solidifi at 75.2°. In between 75.2 and 69.5°, the syste

† Abbreviations: Cr = crystalline solid state; S_A, S_B……S_I = smectic modifications of the type, A, B……I, respectively; nematic phase; Is = isotropic liquid state; cl p. = o'earing point; m.p. = melting point; and tr_1, tr_2… = first, second … transitio in liquid crystalline state.

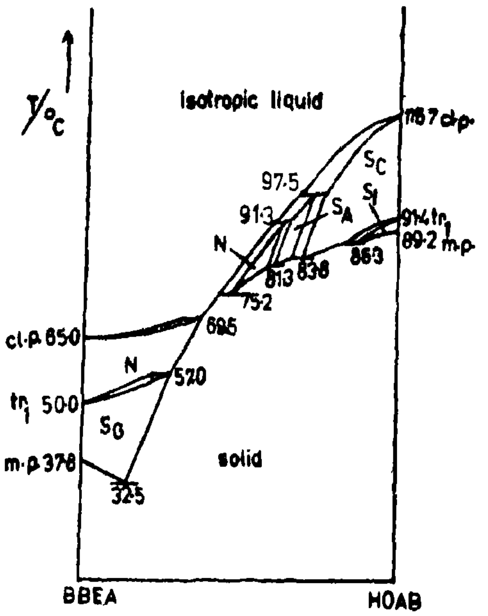


Fig. 1. Binary diagram of state of system HOAB and BBEA.

solidifies directly from isotropic liquid. The eutectic in this binary system is found at 32.5°. Nematic phase on the left hand side does not mix with intermediate nematic phase and has been separated by the solid region.

System 2 (*HOAB*/*HBBA*) : The diagram of state of this binary system is given in Fig. 2. The miscibility between S_C phases present in both the components is not observed. S_C/S_I heterogeneous region shows a maximum at 94.4°. An intermediate phase of the type S_A appears from 98.9 to 81.5°

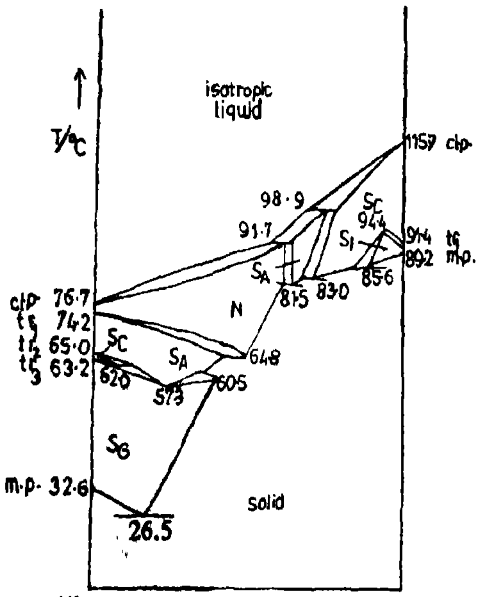


Fig. 2. Binary diagram of state of system HOAB and HBBA.

which does not extend itself to provide any miscibility with the S_A phase of HBBA. Eutectic is obtained at 26.5°.

System 3 (*HOAB*/*HBOA*) : The smectic C phases of HOAB and HBOA as well as S_I phase of HOAB give similar results as system 2. Smectic A phase extends itself and possesses the largest area in this diagram of state. Although S_B and S_G modifications extend themselves, but are suppressed by the presence of existence of S_A phase. Nematic phase appears as an intermediate phase at 89.5° through a three-phase reaction, isotropic liquid+$S_A \leftrightarrow$N as shown in Fig. 3. The heterogeneous region of N$-S_A$ has a minimum at 78.2°.

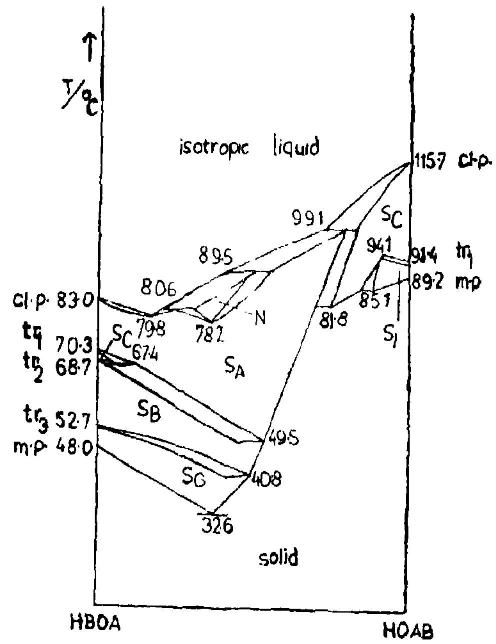


Fig. 3. Binary diagram of state of system HOAB and HBOA.

Thus in all these systems, HOAB was mixed with different substances of the homologous series of *N*-[4-n-alkyloxy-benzylidene]-4'-n-alkylaniline. The substances of this homologous series possess S_C, S_B and S_G phases in addition to N and S_A phases in some of their derivatives. The smectic B and smectic G phases of this homologous series and smectic I phase of HOAB remain restricted on their respective sides. In all the systems, except system 1, a maximum in the heterogeneous region of S_C and S_I phases have been observed. The intermediate phases of the type N and S_A have been observed in systems 3 and 2, respectively, while in system 1, both nematic as well as smectic A appear as intermediate phases. The existence of intermediate nematic phase in systems 1 and 3 can be interpreted due to the existence of nematic phase in heptyl and lower homologous of the series *N*-[4-n-heptyloxy-benzylidene]-4'-n-alkylaniline. The appearance of intermediate S_A phase in these systems can be explained from the existence of S_A phase in other

homologous of *N*-[4-4-n-alkyloxy-benzylidene]-4'-n-alkylaniline. The intermediate phases of N and S_A types do *not* show *any miscibility* with N and S_A modifications present on the left hand side of these diagrams of state. It may be possible that the crystallization front from pure HOAB does not allow the intermediate phases to extend their regions. Further, HOAB does not show much undercooling. S_A phase also does not appear in other homologous series of 4,4'-bis-n-alkadecyloxy-azoxybenzene.

An intermediate S_C modification, which is tilted to the layers, has been observed in the binary system of 4,4'-bis-[n-octadecyl-amino]-biphenyl and n-amyl-4-[4'-n-dodecyloxy-benzylidene-amino]-cinnamate[1]. S_B phase also appears as an intermediate phase in the binary systems between n-amyl-4-[4'-n-dodecyloxy-benzylidene-amino]-cinnamate and 4,4'-bis-[n-decyl-amino]-biphenyl and between C_9/C_{18} and C_{10}/C_{18} homologous of 4,4'-bis-[n-alkyl-amino]-biphenyl and 4,4'-bis-[n-octadecyl-amino]-biphenyl[1], respectively.

References

1. N. K. Sharma, W. Weissflog, L. Richter, S. Diele, B. Walther, H. Sackmann and D. Demus in "Advances in Liquid Crystal Research and Applications", ed. Lajos Bata, Pergamon Press, Oxford, 1980, Vol. 1, p. 3.
2. K. Araya and Y. Matsunaga, *Mol. Cryst. Liq. Cryst.*, 1981, **67**, 153.
3. N. K. Sharma, G. Pelzl, D. Demus and W. Weissflog, *Z. Phys. Chem.*, 1980, **261**, 579.
4. F. Schneider and N. K. Sharma, *Z. Naturforsch.*, *Teil A*, 1981, **36**, 62.
5. D. Demus, H. Demus and H. Zaschke, "Fluessige Kristalle in Tabellen", VEB Deutscher Verlag fuer Grundstoffindustrie, Leipzig, 1976.
6. N. K. Sharma, "Untersuchung Der Polymorphie Smektischer Fluessiger Kristalle", Martin Luther University, 1979.
7. L. Richter, Dissertation, Martin Luther University, 1980.
8. A. J. Leadbetter, M. A. Majid, B. A. Kelly, J. W. Goodby and G. W. Gray, *Phys. Rev. Lett.*, 1979, **43** 9.
9. D. Demus, J. W. Goodby, G. W. Gray and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, 1980, 56, 311.
10. L. Koffler and A. Koffler, "Thermo-Mikromethoden Zur Kennzeichnung Organischer stoffe und Stoffgemische", Verlag Chemie, Weinheim, 1954.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 670-672

Studies on Interaction of Acid Bentonite with Aluminium Hydroxide Gel

M. ADHIKARI, M. K. MAJUMDAR and T. K. SEN

Department of Agriculture, University of Calcutta, Calcutta-700 019

Manuscript received 2 May 1983, revised 4 April 1984, accepted 21 July 1984

The nature of acidity of a freshly prepared colloidal H-bentonite and its changes on aging and interaction with aluminium hydroxide gel have been evaluated from electrometric titrations. Fresh H-bentonite shows two acid species H_3O^+ (57 me) and $Al(H_2O)_6^{3+}$ (22 me). On aging three acid species, H_3O^+ (23 me), $Al(H_2O)_6^{3+}$ (35 me) and hydroxy-Al polymers (21 me) are observed. Interaction of fresh H-clay with hydroxy-Al gel produces only one type of acidity (75 me). In *X*-ray diffraction pattern, the basal spacing of fresh H-bentonite 13.88 Å shifts to 15.36 Å (diffuse band) in gel treated H-clay mixture. On glycerol treatment 18.06 Å of H-bentonite shifts to 17.16 Å in gel treated H-clay mixture. In DTA curve dehydration peak temperature, 150°, of H-bentonite shifts to 130° in gel treated H-clay mixture. The dehydroxylation peak temperature 570°, of H-clay is lowered to 555° in gel treated mixture. Such differences are explained as due to fixation of hydroxy-aluminium in interlayer spaces in the unit cell structure of clay.

PREVIOUS studies[1-10] on acid clays have identified exchangeable H_3O^+ and $Al(H_2O)_6^{3+}$, $(AlOH)^{2+}$ *etc* as active acid species which hydrolyse on aging with time to polymeric hydroxy-aluminium behaving as potential or latent acid species (Bronsted type). This investigation has been undertaken to understand the nature of titratable acidities of a fresh acid clay and of an aged acid clay and that of interaction product of acid clay with synthetic aluminium hydroxide gel.

Experimental

The clay material was $<2\mu$ fraction isolated from a bentonite sample (Rajasthan) by the usual method[11] of dispersion and sedimentation. H-bentonite was obtained by passing Ca-bentonite through a column of H-resin (IR-120, Amberlite). The structural formula of the clay mineral was obtained from the data on chemical analysis by standard methods[12].

One portion of the H-clay was immediately titrated with NaOH. Another portion was allowed to age for 4 weeks before subjecting it to titration with NaOH. The mixture of H-clay and $Al(OH)_3$ gel was prepared by mixing H-clay with that portion of $Al(OH)_3$ gel as being equivalent in terms of Al^{3+} to the amount released on aging the H-clay for 4 weeks. The mixture was allowed to age for 4 weeks before titration. The $Al(OH)_3$ gel was prepared by adding 0.1 *N* NaOH to requisite amount of $AlCl_3$ (AnalaR) and freed from NaCl. The *p*H of the prepared gel was 6.0. The temperature during experiment was maintained at 30°±0.5. For titration[5] of these three systems 0.5% suspensions were taken separately and equilibrated for 24 h with increasing amounts of 0.02 *N* NaOH. The *p*H and conductance were measured after equilibration. The results are shown in Fig. 1.

The *X*-ray analyses[13] of air-dried clay samples were done on Philips model 1010 (Cu target, Ni filter) with 11.54 cm Debye-Scherrer camera. Lattice spacings and intensities of the lines are given in Table 1.

Differential thermal analyses[14] of air-dried fresh and aged bentonite samples and of the clay-gel mixture are shown graphically in Fig. 2.

Results and Discussion

The chemical composition of H-bentonite, the charge distribution in unit cell structure, and the formula of the mineral (assumed to be composed of montmorillonite alone) are given below :

Analysis of acid bentonite: SiO_2, 52.40 ; Al_2O_3, 20.20 ; Fe_2O_3, 4.5 ; TiO_2, 0.20 ; MgO, 2.80 ; Na_2O, 0.20 ; K_2O, 0.10 ; H_2O, 19.50 % ; H^+, 78 me ; SiO_2/Al_2O_3, 4.36.

Charge distribution in component layers of unit cell structure of H-clay : tetrahedral (Si, Al), —1.58 ; octahedral (Al, Fe^{III}, Mg), 0.72 ; non-exchangable cation, 0.07 ; net unbalanced, —0.79 ; exchangable H^+, 0.70.

Structural formula of clay mineral in clay fraction of bentonite : $[(Si_{7.62}\ Al_{0.38})\ (Al_{3.11}\ Fe^{III}_{0.42}\ Ti_{0.02}Mg_{0.10})\ (Na_{0.05}K_{0.02})]^{-0.79}H^{+0.79}$.

The titration curves in Fig. 1 reveal that fresh H-bentonite is dibasic in nature, showing two inflections at *p*H 6.25 and 8.6, and two breaks

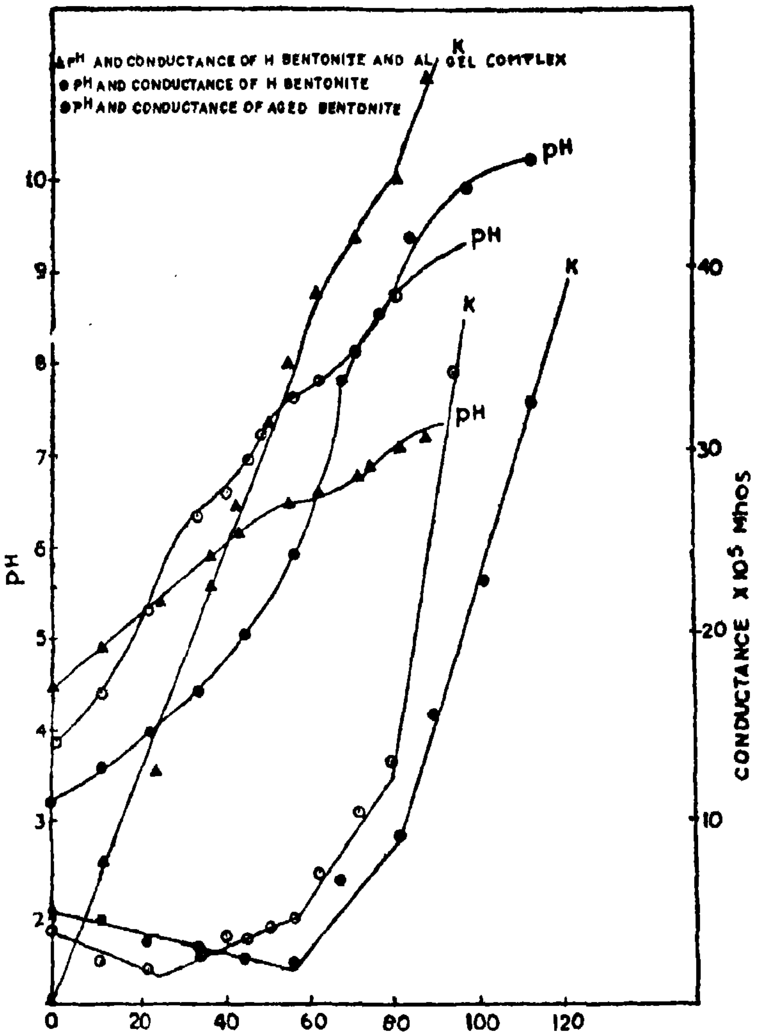


Fig. 1. me of NaOH per 100 g of clay.

TABLE 1—X-RAY POWDER DIFFRACTION DATA

H-bentonite d	H-bentonite I	Aged H-bentonite d	Aged H-bentonite I	Al-gel treated bentonite d	Al-gel treated bentonite I	Glycerol treated H-bentonite d	Glycerol treated H-bentonite I	Glycerol treated aged H-bentonite d	Glycerol treated aged H-bentonite I	Glycerol treated Al-gel-interacted bentonite d	Glycerol treated Al-gel-interacted bentonite I
13 88	s	15.06	m(bd)	15.36	bd	18.06	ms	17.85	ms	17.16	ms
10.08	w	9.98	w	9.90	vvw	10.10	w	9.77	vvw	9.81	vw
7.02	vs	7.06	ms	7.01	w	7.10	ms	7.07	s	7.10	ms
4.65	s	4.58	vw	4.55	mw	4.53	w	4.45	w	4.83	vw
3.56	vw	3.56	w	3.66	vvw	3.60	vw	3.60	vw	3.68	w
2.50	mw	2.50	w	2.45	vvw	—	—	—	—	—	—

d = interplaner spacing (Å), I = relative intensity.
vvs = very very strong, vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, vvw = very very weak, bd = broad diffuse.

in conductance at 0.7 and 3.5μ mho. The corresponding acidities are due to 57 me H_3O^+ and 22 me $Al(H_2O)_6^{3+}$ per 100 g H-clay. The aged clay sol (4 weeks), in contrast, gives three inflections and breaks in potentiometric and conductometric titration curves, respectively. The inflections at *p*H 5.2 and 7.0 are due to neutralisation of 23 me H_3O^+ and 35 me $Al(H_2O)_6^{3+}$, respectively. The inflection at 8.6 is due to neutralisation of polymeric hydroxy-Al (latent acidity) on aging for 4 weeks.

H-bentonite loses 35 me H_3O^+ions which migrate from exchange sites to the edges where they attack

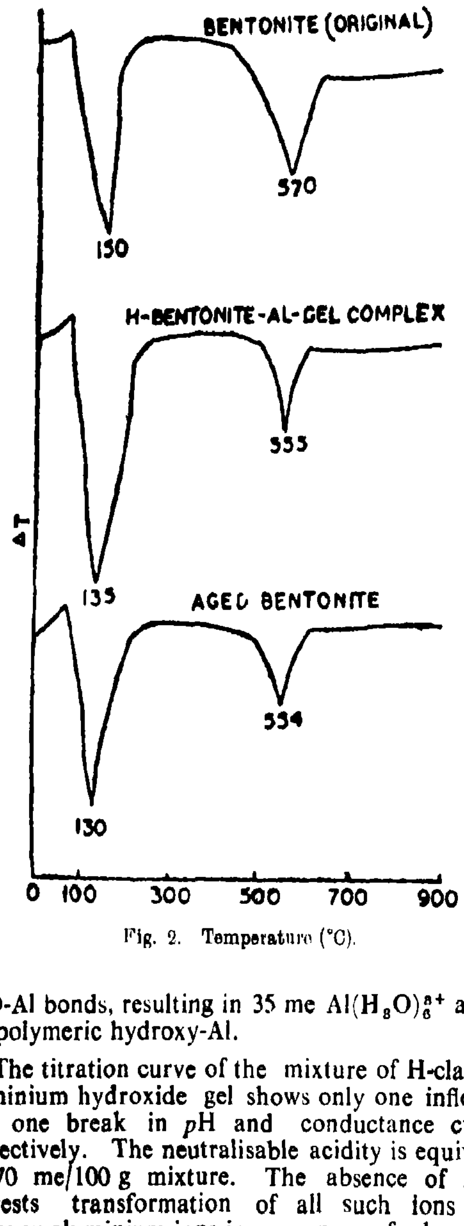


Fig. 2. Temperature (°C).

Si-O-Al bonds, resulting in 35 me $Al(H_2O)_6^{3+}$ and 21 me polymeric hydroxy-Al.

The titration curve of the mixture of H-clay and aluminium hydroxide gel shows only one inflection and one break in *p*H and conductance curves, respectively. The neutralisable acidity is equivalent to 70 me/100 g mixture. The absence of H_3O^+ suggests transformation of all such ions into hydroxy-aluminium ions in presence of aluminium hydroxide gel. The monotonous rise of conductance on titration points to a similar conclusion. The total alkali need to titrate fresh H-bentonite and aged bentonite is 79 me but for Al-gel and bentonite mixture it is 75 me/100 g mixture. Thus a decrease of 4 me/100 g is due to fixation of hydroxy-Al on exchange sites.

Differential thermal curves for fresh and aged bentonite, and for aluminium hydroxide gel-bentonite mixture are given in Fig. 2, which show endothermic dehydration peaks at 150, 135, and 130°, respectively for hygroscopic moisture and interlayer water loss. The endothermic dehydroxylation peak temperature for fresh bentonite at 570° is similarly lowered to 555° in the case of aged bentonite and gel-bentonite mixture. Such lowering in mixed system is known[8]

The mineralogical characteristics of H-bentonite alter both on aging and on interaction with synthetic gel. The *X*-ray diffraction diagram show that the basal spacing 13.88 Å of H-bentonite shifts to 15.06 Å (diffuse band) for aged bentonite and to 15.36 Å (diffuse band) for gel-bentonite mixture (Table 1). This indicates that coating with hydroxy-aluminium polymers interferes in the *X*-ray diffraction pattern[6]. On the other hand, in glycerol treated H-bentonite the basal spacing increases to 18.06 Å, whereas it is 17.85 Å for aged bentonite and 17.16Å for gel-bentonite mixture. A weak line at about 10 Å in H-bentonite may be due to a small quantity of biotite.

References

1. H. PAVER and C. E. MARSHALL, *J. Soc. Chem. Ind.*, 1934, **53**, 750.
2. J. N. MUKHERJEE and R. P. MITRA, *J. Colloid Sci.*, 1946, **1**, 141.
3. C. E. MARSHALL, "The Colloid Chemistry of the Silicate Minerals", Academic Press, New York, 1949.
4. A. K. GANGULY and S. K. MUKHERJEE, *J. Phys. Colloid Chem.*, 1951, **55**, 1429.
5. M. ADHIKARI, *J. Indian Soc. Soil Sci.*, 1958, **6**, 147.
6. R. P. MITRA and H. SINGH, *Naturwissenschaften*, 1959, **9**, 814.
7. N. T. COLEMAN and D. CRAIG, *Soil Sci.*, 1961, **91**, 14.
8. M. L. JACKSON and U. SCHWERTMAN, *Soil Sci. Soc. Am. Proc.*, 1964, **28**, 179.
9. R. C. DALAL, *Soil Sci.*, 1975, **119**, 2, 127.
10. P. VIOLANTE and A. VIOLANTE, *Soil Sci.*, 1978, **126**, 136.
11. C. S. PIPER, "Soil and Plant Analysis", University of Adelaide, Australia, 1950.
12. A. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longmans Green, London, 1969.
13. "The *X*-Ray Identification and Crystal Structures of Clay Minerals" ed. G. BROWN, Minerological Society, London, 1961.
14. "Differential Thermal Analysis", ed. R. C. MACKENZIE, Academic Press, 1970.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 673-676

Rheological Properties of Some Binary Organic Systems

G. P. SACHDEV, B. L. SHARMA, N. K. SHARMA* and P. S. BASSI**

Department of Chemistry, University of Jammu, Jammu-180 001

Manuscript received 3 May 1983, accepted 21 July 1984

The viscosities and activation energies for the binary naphthalene-p-dichlorobenzene and naphthalenediphenylamine eutectic melts were found to be more than pure components and off-eutectic mixtures. This is explained on the basis of microregions rich in one or the other component. In naphthalene-thymol system viscosity at eutectic shows a decrease, whereas activation energy shows an increase in passing from one component to the other. This decrease is attributed to the breaking of hydrogen bonds in thymol molecule. Strength of interaction in these binary systems as obtained from viscosities of mixing shows a weak interaction in all the three systems.

VISCOSITY measurements have turned out to be an effective tool to investigate the structure of liquids. Pluss[1], Fisher *et al.*[2] and Jones *et al.*[3] have observed anomalously low viscosities of molten Pb-Sn at eutectic composition. Dutchak and Panasyuk[4] found that the kinematic viscosity of Bi-Sb alloys followed the exponential form. Wilson[5] pointed out that many systems exhibited a sharp minimum in viscosity at eutectic composition in both Pb-Sn and Pb-Sb melts that could not be found by Gebhardt *et al.*[6] The viscosity of Pu-Fe eutectic alloy has been measured as a function of temperature by Jones *et al.*[7] Higher activation energy for viscous flow than their pure components has been reported.

In view of the anomalous behaviour of viscosities in binary systems, the work on the viscosities of certain binary organic systems giving faceted-faceted crystal morphologies was undertaken. The studies on the viscosities of naphthalene-*p*-dichlorobenzene, naphthalene-thymol and naphthalene-diphenylamine are presented in this paper.

Experimental

Naphthalene (B.D.H.) was purified by ordinary distillation followed by slow sublimation in a china dish at 233 K. *p*-Dichlorobenzene (B.D.H.) was purified by repeated distillation and the distillate was collected at 447-451 K under normal pressure. Diphenylamine (E. Merck, A.R.) was distilled under a pressure 22 mm at 452 K. Thymol (Schering, A.G.) was purified by repeated crystallization with absolute ethanol and kept in a vacuum desiccator for about a week. The melting points of purified materials, *i.e.* naphthalene (353.3 K), *p*-dichlorobenzene (326.7 K), diphenylamine (326.4 K) and thymol (322.8 K) are in good agreement with the literature values.

Determination of viscosity : Viscosities of mixtures and pure components were determined at various temperatures near their melting points. For this purpose, a modified Ostwald's viscometer was used to note the time of flow for a given volume, which was kept constant in each case and gave fairly good results when the kinetic energy correction was applied. The accuracy was verified using a liquid of known viscosity and density at different temperatures. Specific gravity bottles with fine capillaries were used to find the densities in the molten state at the same temperatures. All the measurements were made in a thermostat (accuracy $\pm 0.05^{\circ}$).

Results and Discussion

Viscosity measurements are important in elucidating the nature of the liquid eutectic. Such studies can throw much light on the state of aggregation in the liquid and the presence of any type of specific interactions.

The viscosities of naphthalene-*p*-dichlorobenzene, naphthalene-diphenylamine and naphthalene-thymol systems over the whole range of compositions as different temperatures were determined. There wat a decrease in viscosities with the rise in temperature for pure components, as well as, their mixtures. Viscosities were determined at 353 K (m.p. of naphthalene) and at lower temperatures. The viscosities at 353 K are given in Table 1. There is a decrease in the viscosities at 353 K in naphthalene-*p*-dichlorobenzene system, whereas an increase in the viscosities at 353 K for the systems naphthalene-thymol and naphthalene-diphenylamine is observed (Table 1). Fig. 1 represents the curves of viscosities (η) at 353 K against mole fraction of naphthalene for the three binary systems. It is evident that when one component is added to the other, the viscosity of the mixture rises and falls gradually for naphthalene-*p*-dichlorobenzene and naphthalene-diphenylamine systems, respectively. But at the eutectic composition, there is a sudden increase in the value of viscosity as indicated by the

** Department of Chemistry, Guru Nanak Dev University, Amritsar-143 005.

TABLE 1—VISCOSITIES AND ACTIVATION ENERGIES FOR VISCOSITIES OF SYSTEMS AT 358 K

Naphthalene-p-dichlorobenzene			Naphthalene-thymol			Naphthalene-diphenylamine		
Mole fraction of p-dichlorobenzene	η (cp)	E_{vis} × 10^{-3} cal mol^{-1}	Mole fraction of thymol	η (cp)	E_{vis} × 10^{-3} cal mol^{-1}	Mole fraction of diphenylamine	η (cp)	E_{vis} × 10^{-3} cal mol^{-1}
0.0000	0.9661	3.21	0.0000	0.9661	3.21	0.0000	0.9661	3.21
0.1989	0.8716	2.76	0.2000	0.9795	3.88	0.1380	1.0096	3.25
0.4000	0.7889	2.62	0.4000	1.0918	4.55	0.4002	1.3277	4.57
0.5000	0.7834	2.78	0.5000	1.1847	4.58	0.6005	1.6254	6.33
0.5500	0.7227	2.82	0.6000	1.3031	5.24	0.6350^e	1.7358	6.78
0.6110^e	0.7139	2.46	0.6990^e	1.3688	5.69	0.7001	1.7828	6.11
0.6500	0.6984	2.40	0.8000	1.4952	6.58	0.8001	2.0578	6.10
0.7000	0.6809	2.43	1.0000	1.7670	7.38	1.0000	2.5270	6.68
0.8002	0.6409	2.48						
1.0000	0.5903	2.86						

e = eutectic.

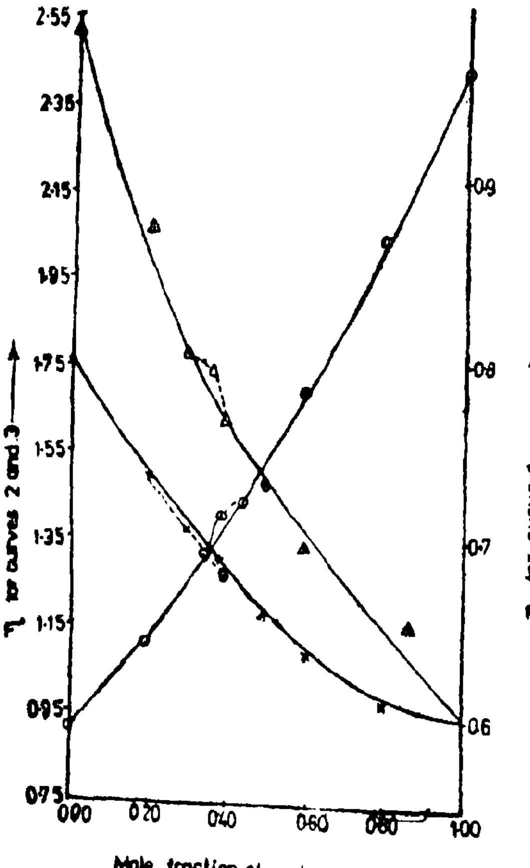


Fig. 1. Plot of viscosity *vs.* composition at 358 K for (1) naphthalene-p-dichlorobenzene, (2) naphthalene-diphenylamine, (3) naphthalene-thymol systems.

dotted lines in curves 1 and 3 (Fig. 1). Similar point of inflection at the eutectic concentration was observed in Bi-Sb alloys[6]. Points of inflection at eutectic temperatures have been observed in all the three binary systems. No significant increase or decrease in the viscosities, *i.e.* no point of inflection, has been observed at the eutectic composition of α-naphthylamine-diphenylamine system[9]. The viscosity at eutectic in naphthalene-diphenyl system[10] possessed a maximum value.

The eutectic mixture of naphthalene-thymol system behaves differently. When naphthalene is added to thymol, the viscosity falls gradually but at the eutectic composition the viscosity decreases instead of increasing (curve 2, Fig. 1). Some workers have also observed a minimum at the eutectic composition in some systems[2,3,5]. This anomalous behaviour of eutectic melt could not be explained. The deviation in the behaviour of naphthalene-thymol eutectic from the eutectics of other systems is due to thymol. Thymol is highly viscous due to the presence of very strong hydrogen bonding in the liquid state. With the addition of naphthalene to thymol, the hydrogen bonds between the molecules of thymol break effecting the decrease in viscosity. At the eutectic composition, it appears that the clustering effect as observed in the other systems is insignificant. Since the eutectic mixture of naphthalene-thymol system contains a small fraction of naphthalene (0.301 mol), the thermal motion of the molecules does not allow the molecules of naphthalene to come closer and form clusters. In the eutectic melt of this system no other interaction except the breaking of hydrogen bonds seems to occur. The viscosities of pure components and various other mixtures were determined as a function of temperature. The results obey the following equation :

$$\eta = \eta_0 e^{E_{vis}/RT} \qquad (1)$$

where η_0 is constant, E_{vis} is activation energy for viscous flow. Fig. 2. 3 and 4 give log η *vs.* 1/T plots of naphthalene-p-dichlorobenzene, naphthalene-diphenylamine and naphthalene-thymol, respectively. The activation energies obtained from these figures are given in Table 1. The activation energy in the naphthalene-p-dichlorobenzene shows a decrease upto 0.55 mole fraction of p-dichlorobenzene, increases to 2.46 × 10^{-3} cal mol^{-1} at the eutectic and decreases again to 2.40 × 10^{-3} cal mol^{-1} at 0.65 mole fraction. Furthermore, the activation energy

6.73×10^{-8}, the maximum value, has been found in the eutectic of naphthalene-diphenylamine. A gradual increase in the activation energy of pre-eutectic and decrease in the post-eutectic composition has been observed.

The higher value of viscosity and the activation energies for viscous flow for eutectic melt can be explained on the basis of structural changes occurring in the eutectic liquid, which may be assumed to consist of micro-regions or groups rich in one component or the other. Such grouping of atoms in an ordered array would produce an increase in viscosity and consequently in activation energy. As the temperature of the liquid eutectic is raised, the degree of clustering goes on diminishing. Thus two factors will contribute to the activation energy of the eutectic mixtures: (i) activation energy for viscous flow, and (ii) energy required for breaking the clusters. In case of pure components, no energy is needed for breaking the clusters. Hence, activation energy for pure components should be less than that of their mixtures.

The activation energy and viscosity for the eutectic mixture should be maximum as it contained maximum clusters, eutectic melt being formed at the lowest temperature with definite composition. Also, the activation energy in the case of eutectic should go on decreasing with the rise in temperature as more and more of clusters break. At a temperature, when all the clusters have been broken, only first factor will contribute to E_{vis}.

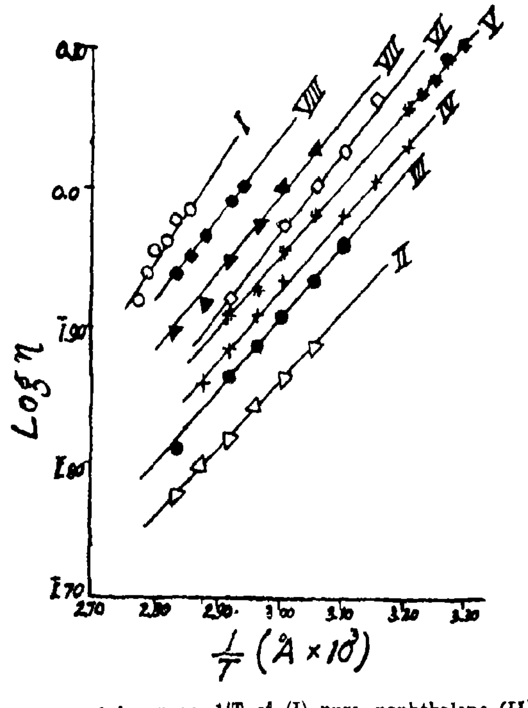


Fig. 2. Plot of log η vs. 1/T of (I) pure naphthalene, (II) pure d-dichlorobenzene, and (III) to (VIII) mixtures with 0.80, 0.70, 0.611 (eutectic), 0.60, 0.40 and 0.20 mole fractions of p-dichlorobenzene, respectively.

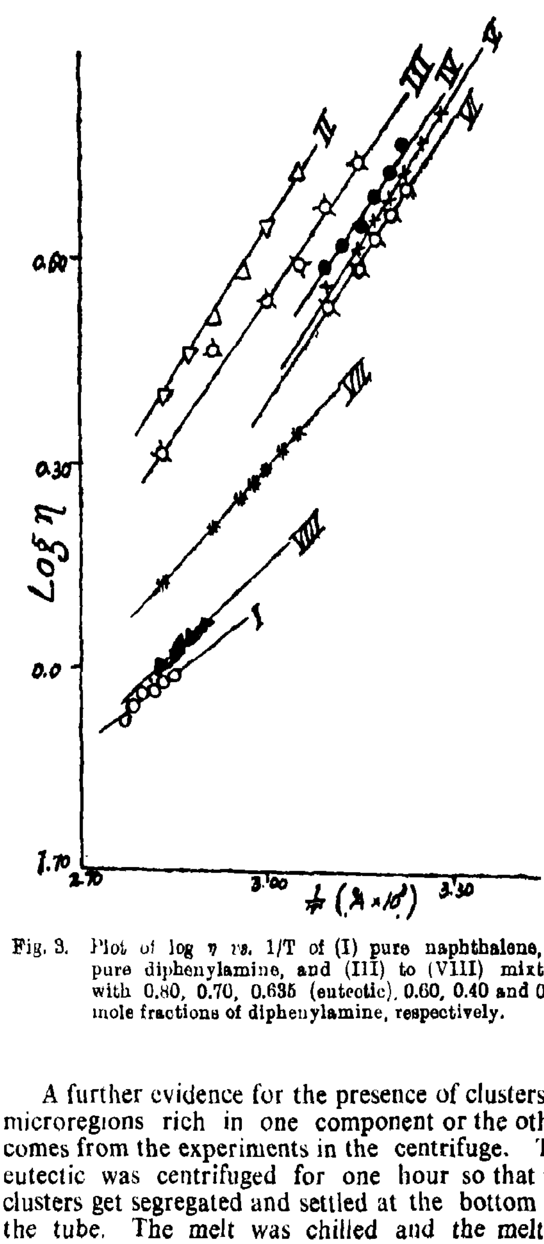


Fig. 3. Plot of log η vs. 1/T of (I) pure naphthalene, (II) pure diphenylamine, and (III) to (VIII) mixtures with 0.80, 0.70, 0.635 (eutectic), 0.60, 0.40 and 0.138 mole fractions of diphenylamine, respectively.

A further evidence for the presence of clusters or microregions rich in one component or the other, comes from the experiments in the centrifuge. The eutectic was centrifuged for one hour so that the clusters get segregated and settled at the bottom of the tube. The melt was chilled and the melting points determined at different distances from the bottom of the tube. They differ from the eutectic temperature showing that the eutectic solid consists of areas rich in one component or the other. This leads to the presence of such regions in the eutectic liquid.

Activation energy shows a steady increase in the naphthalene-thymol system indicating that no micro-regions in this system are formed.

Determination of interaction in binary system : The viscosity data can be used to know about the complexing tendency of binary mixtures. The strength of interactions in binary mixtures have been estimated from the expression[11]:

$$\ln \eta_{mix} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 . d. \qquad (2)$$

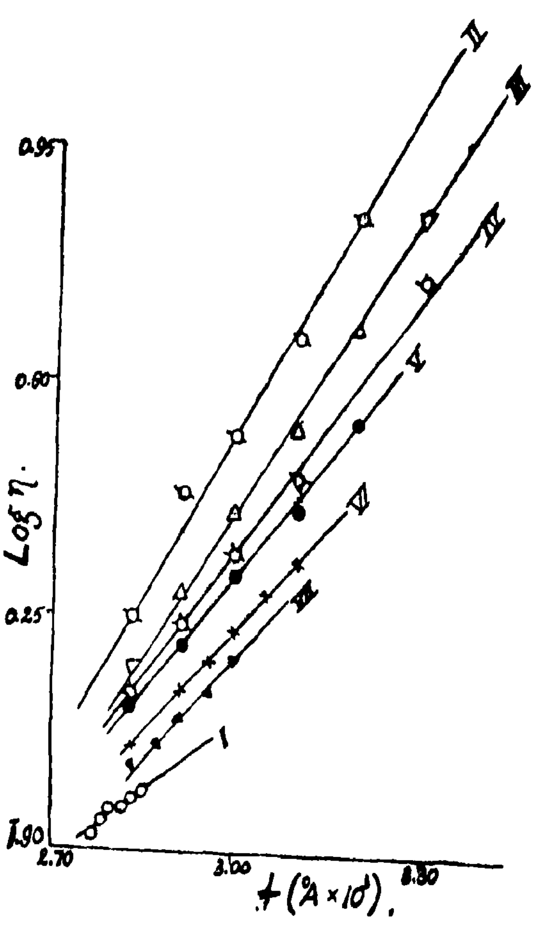


Fig. 4. Plot of log η vs. 1/T of (I) pure naphthalene, (II) pure thymol, and (III) to (VIII) mixtures with 0.80, 0.699 (eutectic mixture), 0.60, 0.50, 0.40 and 1.20 mole fractions of thymol, respectively.

where η_{mix}, η_1 and η_2 are experimental viscosities of mixtures, component 1 and component 2, respectively. x_1 and x_2 are the mole fractions of the corresponding components, and d is proportional to W/RT and may be regarded as approximate measure of strength of interaction between the components, W is the interchange energy.

Excess viscosity is given by the following equation :

$$\eta_E = \eta_{mix} - (x_1\eta_1 + x_2\eta_2) \quad (3)$$

It was hypothesized[12] that (i) if $\eta_E > 0$ and $d > 0$, then specific interactions would be present ; (ii) if $\eta_E > 0$ and $d < 0$, then weak interactions would be present and (iii) if $\eta_E < 0$ and $d < 0$, then specific interactions would be absent. The values of η_{mix}, η_E and d for the systems naphthalene-*p*-dichlorobenzene, naphthalene-thymol and naphthalene-diphenylamine systems are given in Table 2.

In naphthalene-*p*-dichlorobenzene at eutectic composition $\eta_E < 0$ and $d > 0$ there may be a very

TABLE 2—VISCOSITY OF NAPHTHALENE CONTAINING BINARY MIXTURES AT 353 K

Mole fraction of components B	η_{mix} cp	η_E cp	d
Naphthalene (A)-*p*-dirhlorobenzene (B) system			
0.200	0.8716	0.0045	0.0863
0.400	0.7889	-0.0157	0.0247
0.500	0.7334	-0.0355	-0.0790
0.550	0.7227	-0.0283	-0.0434
0.611*	0.7139	-0.0153	0.0227
0.650	0.6984	-0.0219	-0.0217
0.700	0.6809	-0.0166	0.0041
0.800	0.6498	-0.0119	0.0074
Naphthalene (A)-thymol (B) system			
0.200	0.9795	-0.1820	-0.5718
0.400	1.0918	-0.1835	-0.4474
0.500	1.1847	-0.1726	-0.3518
0.600	1.3031	-0.3981	-0.2806
0.699*	1.3633	-0.1574	-0.3458
0.800	1.4952	-0.1079	-0.2657
Naphthalene (A)-diphenylamine (B) system			
0.198	1.0096	-0.1559	0.0425
0.400	1.3277	-0.2516	-0.2311
0.600	1.6254	-0.2698	-0.2043
0.635*	1.7358	-0.2146	-0.0756
0.700	1.7828	-0.2703	-0.2587
0.800	2.0578	-0.1533	-0.0620

e = eutectic.

weak interaction at this composition, whereas near the eutectic composition $\eta_E < 0$ and $d < 0$, there may not be any interaction in these mixtures. In naphthalene-diphenylamine system although $\eta_E < 0$ and $d < 0$, there is a marked increase in the magnitude of η_E and d at eutectic composition suggesting the presence of weak interactions. Similar observations are made in case of the other system. These weak interactions may be due to the formation of microregions in the eutectic melt.

References

1. M. PLUSS, *Z. Anorg. Allg. Chem.*, 1915, 93.
2. H. J. FISHER and A. PHILLIPS, *Trans. Am. Inst. Mech. Eng.*, 1954, **200**, 1060.
3. W. R. D. JONES and J. B. DAVIES, *J. Inst. Met.*, 1957, **86**, 164.
4. Y. I. DUTCHAK and P. V. PANASYUK, *Phys. Met. Metall.*, 1963, **15**, 1963.
5. J. R. WILSON, *Metall. Rev.*, 1965, **10**, 381.
6. E. GEBHARDT and K. KOSTLIN, *Z. Metallk.*, 1958, **49**, 605.
7. L. V. JONES, D. OFTE, W. G. ROHR and L. J. WITTENBERG, *Trans. Am. Soc. Met*, 1962, **55**, 819.
8. Y. I. DUTCHAK and P. V. PANASYUK, *Phys. Met. Metall.*, 1964, **18**, 147.
9. B. L. SHARMA, N. K. SHARMA and P. S. BASSI, *Z. Phys. Chem. (Leipzig)*, 1984, **265**, 4.
10. P. S. BASSI and G. P. SACHDEV, *Indian J. Chem.*, 1974, **12**, 727.
11. L. GURNBERG and A. H. NISSAN, *Nature (London)*, 1949, **164**, 799.
11. R. K. NIGAM and P. P. SINGH *Indian J. Chem.*, 1971, **9**, 691.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 677-679

Thermodynamics of the Interaction of Bivalent Transition Metal Ions with Phthalanilic Acids

C. L. SHARMA*, R. S. ARYA, S. S. NARVI and V. MISHRA

Department of Chemistry, University of Roorkee, Roorkee-247 667

Manuscript received 30 January 1984, accepted 10 August 1984

The thermodynamic stepwise stability constants, free energy, enthalpy and entropy changes for the formation of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} ions with phthalanilic, 4-methylphthalanilic, 4-methoxyphthalanilic, 4-chlorophthalanilic, 4-bromophthalanilic and 4-nitrophthalanilic acids were determined. Analysis of the data indicated the chelation of phthalanilic acids through nitrogen of secondary amide and carboxylate groups.

AMINO-ACIDS with oxygen and nitrogen donor atoms have been greatly used as ligands in carrying out the thermodynamical studies on their metal complexes perhaps because of their biological importance[1-6], and for finding out the number and strength of bonds and to detect concomitant changes in the structure of the complexes[7-10]. Anilic acids also have the same donor sites but no reference is available on such type of studies with these compounds. The present communication deals with the determinations of thermodynamical stability constants, ΔF, ΔH and ΔS for the interaction of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} with phthalanilic, 4-methylphthalanilic, 4-methoxyphthalanilic, 4-chlorophthalanilic, 4-bromophthalanilic and 4-nitrophthalanilic acids.

Experimental

The experimental set up and methods have been described earlier[9,10]. The measured *p*H values, calibrated from the analytical concentration of perchloric acid and activity coefficient of H^+, agreed[11] within ± 0.004 *p*H units. The accuracy of the instrument was ± 0.02 units. Carbon dioxide free nitrogen presaturated with solvent methanol-water mixture (20%, v/v), was continuously bubbled through the solution to provide an inert atmosphere.

All the chemicals used were of AnalaR grade, methanol was purified by the standard method[12]. Phthalanilic acids were prepared by the reported method[13] and recrystallised from ethanol. The solutions of metal chlorides, ferrous perchlorates, perchloric acid, sodium perchlorate and anilic acids were prepared in methanol-water mixture (20%, v/v). Due allowance for the contraction in volume on mixing the two solvents were made[14,15].

Calculations : The thermodynamic proton-ligand dissociation constants of phthalanilic acids and stability constants of their complexes were determined potentiometrically following the Bjerrum-Calvin titration technique[16,17] as adapted by Irving and Rossotti[18], and employing the correction factors introduced by Van Uitert[19]. The enthalpy (ΔH) and entropy (ΔS) changes were calculated from the temperature coefficient of the equilibrium constant in a medium of 0.1 *M* $NaClO_4$. The calculations were made on DEC-2050 digital computer.

The accuracy of *p*K values of acids and log K values of the complexes is ± 0.02 and ± 0.04 log units, respectively. Therefore, the precisions of ΔH and ΔS are ± 0.56 kcal mol^{-1} and ± 2.4 cal mol^{-1} deg^{-1}, respectively.

Results and Discussion

The values of pK_1 and pK_2 corresponding to the deprotonation of COOH and NH at 22, 30 and 40°, respectively and at ionic strength 0.1 *M* $NaClO_4$ are given in Table 1. The values of formation

TABLE 1—PROTONATION CONSTANTS OF PHTHALANILIC ACIDS IN 0.1 *M* $NaClO_4$ AT DIFFERENT TEMPERATURES

Acids	Temp. °C	pK_1	pK_2
P	22	4.35	11.15
	30	4.25	11.10
	40	4.15	10.90
4-methyl-P	22	4.45	11.30
	30	4.88	11.15
	40	4.33	11.00
4-methoxy-P	22	4.42	11.30
	30	4.87	11.13
	40	4.88	11.00
4-bromo-P	22	4.15	11.15
	30	4.10	11.00
	40	4.00	10.88
4-chloro-P	22	4.10	11.10
	30	4.00	10.95
	40	3.90	10.85
4-nitro-P	22	3.80	10.90
	30	3.65	10.85
	40	3.55	10.70

P = Phthalanilic acid.

* Vikas Nagar, 134/3, University of Roorkee, Roorkee-247 667.

TABLE 2—THERMODYNAMIC STABILITY CONSTANTS OF METAL COMPLEXES OF PHTHALANILIC ACIDS AT DIFFERENT TEMPERATURES

Acids	Formation constants	Temp.	Mn^{II}	Fe^{II}	Co^{II}	Ni^{II}	Cu^{II}
P	Log T_{K_1}	22	5.30	10.90	5.40	5.25	8.30
		30	5.25	10.70	5.35	5.20	8.15
		40	5.15	10.45	5.25	5.10	8.00
	Log T_{K_2}	22	4.55	7.75	4.55	4.45	7.25
		30	4.50	7.65	4.50	4.40	7.20
		40	4.45	7.55	4.45	4.35	7.10
	Log T_{β_2}	22	9.85	18.65	9.95	9.70	15.55
		30	9.75	18.35	9.85	9.60	15.35
		40	9.60	18.00	9.70	9.45	15.10
4-methyl-P	Log T_{K_1}	22	6.40	11.95	6.85	7.50	9.25
		30	6.30	11.65	6.75	7.40	9.00
		40	6.20	11.35	6.65	7.25	8.80
	Log T_{K_2}	22	5.15	9.35	5.20	5.65	7.90
		30	5.10	9.20	5.15	5.60	7.80
		40	5.05	9.05	5.10	5.50	7.70
	Log T_{β_2}	22	11.55	21.30	12.05	13.15	17.15
		30	11.40	20 85	11.90	13.00	16.80
		40	11.25	20.40	11.75	12.75	16.50
4-methoxy-P	Log T_{K_1}	22	7.65	10.80	8.60	8 60	9 65
		30	7.55	10.50	8.45	8.45	9.40
		40	7.45	10.20	8.30	8.30	9.15
	Log T_{K_2}	22	5.50	9.60	6.40	6.40	7.75
		30	5.45	9.40	6.30	6.30	7.60
		40	5.40	9.20	6.20	6.20	7.45
	Log T_{β_2}	22	13.15	20.40	15.00	15.00	17.40
		30	13.00	19.90	14.75	14.75	17.00
		40	12.95	19.40	14.50	14.50	16.60
4-chloro-P	Log T_{K_1}	22	6.40	11.20	7.40	7.50	9.80
		30	6.35	10.95	7.30	7.40	9.60
		40	6.25	10.70	7.20	7.25	9.35
	Log T_{K_2}	22	4.45	8.15	5.10	5.20	8.15
		30	4.40	8.00	5.05	5.15	8.05
		40	4.35	7.85	5.00	5.05	7.95
	Log T_{β_2}	22	10 85	19.35	12.50	12.70	17.95
		30	10.75	18.95	12.35	12.55	17.65
		40	10.70	18.55	12.20	12 30	17.30
4-bromo-P	Log T_{K_1}	22	6.45	11.20	7.40	7.55	9.30
		30	6.35	11.00	7.30	7.45	9.15
		40	6.25	10.75	7.20	7.35	9.00
	Log T_{K_2}	22	4.80	8.40	5.40	5.50	8 05
		30	4.75	8.25	5.35	5.45	7.95
		40	4.70	8.10	5.30	5.40	7.85
	Log T_{β_2}	22	11.25	19.60	12.80	13.05	17.35
		30	11.10	19.25	12.65	12.90	17.10
		40	10.95	18.85	12.50	12.75	16.85
4-nitro-P	Log T_{K_1}	22	6.60	11.95	7.05	6.60	8.75
		30	6.55	11.65	6.95	6.50	8.55
		40	6.45	11.35	6.85	6.40	8.35
	Log T_{K_2}	22	5.30	8.80	5.60	5.50	7.45
		30	5.25	8.65	5.55	5.45	7.30
		40	5.20	8.50	5.50	5.40	7.15
	Log T_{β_2}	22	11.90	20.75	12.65	12 10	16.20
		30	11.80	20.30	12.50	11.95	15.85
		40	11.65	19.85	12.35	11.80	15.50

P = Phthalanilic acid.

constants are given in Table 2 and the values of ΔF, ΔH and ΔS corresponding to first, and second step reactions are given in Table 3. The pK_1 and pK_2 were found to have the following order.

4-methoxy-P≈4-methyl-P > P > 4-bromo-P > 4-chloro-P > 4-nitro-P

Thus the deprotonation of COOH and NH is affected by inductive and mesomeric effects of the substituents. The electron density at the reaction centre is reduced by the electron attracting groups in the order, NO_2 > Cl > Br. Hence, the liberation of the proton becomes easier in the same order while reverse is true in 4-methyl and 4-methoxy derivatives.

TABLE 3—Stepwise ΔF^0 at 22° and ΔH Values (kcal mole^{-1}), and ΔS Values in (cal mol^{-1} deg^{-1}) at 30°

Acids	Thermodynamic parameter	Mn^{II}	Fe^{II}	Co^{II}	Ni^{II}	Cu^{II}
P	$-\Delta F_1^0$	29.50	61.00	30.12	29.25	46.32
	$-\Delta F_2^0$	26.44	44.22	26.44	25.52	41.30
	$-\Delta H_1$	10.54	46.65	12.30	12.30	29.75
	$-\Delta H_2$	9.58	26.40	9.87	9 87	16.86
	ΔS_1	64.22	39.62	60.83	57.45	55.94
	ΔS_2	57.03	60.88	56.07	58.18	82.72
4-methyl-P	$-\Delta F_1^0$	35.61	66.99	37.87	41.92	51.97
	$-\Delta F_2^0$	29.37	53.26	29.96	32.76	45.19
	$-\Delta H_1$	17.95	60.38	18.24	24.10	42.55
	$-\Delta H_2$	13.39	32.80	13.63	14.73	19.16
	ΔS_1	59.79	22.22	66.27	60.50	31.46
	ΔS_2	53.97	69.45	64.98	61.04	88.24
4-methoxy-P	$-\Delta F_1^0$	42.59	60.46	47.78	47.74	53.68
	ΔF_2^0	31.34	54.52	36.74	36.11	44.64
	$-\Delta H_1$	18.37	53.60	25.52	27.36	49.62
	$-\Delta H_2$	11.59	33.05	16.23	14.94	26.90
	ΔS_1	82.01	22.64	75.40	69.04	13.51
	ΔS_2	86.82	72.34	69.33	71.25	60.21
4-chloro-P	$-\Delta F_1^0$	35.86	62.51	41.00	41.55	54.68
	$-\Delta F_2^0$	26.11	46.44	29.20	29.83	46.48
	$-\Delta H_1$	15.52	49.33	21.00	22.97	42.89
	$-\Delta H_2$	9.58	28.70	10.54	12.30	22.59
	ΔS_1	68.78	44.60	67.78	62.97	39.75
	ΔS_2	55.94	59.91	63.26	59.37	80.92
4-bromo-P	$-\Delta F_1^0$	36.11	62.80	41.95	41.80	52.09
	$-\Delta F_2^0$	27.49	47.91	30.88	31.51	44.85
	$-\Delta H_1$	14.73	51.42	15.94	18.24	31.21
	$-\Delta H_2$	8.49	30.63	8.49	10.54	18.37
	ΔS_1	72.34	38.37	85.77	79.96	70.71
	ΔS_2	64.48	58.41	75.94	71.13	89.62
4-nitro-P	$-\Delta F_1^0$	36.82	66.99	39.83	36.74	48.70
	$-\Delta F_2^0$	30.21	50.38	31.84	31.51	42.63
	$-\Delta H_1$	15.31	57.20	18.33	17.74	39.75
	$-\Delta H_2$	7.99	31.71	12.30	9.87	24.98
	ΔS_1	72.93	32.72	71.13	64.35	30.25
	ΔS_2	75.27	03.20	66.27	73.30	59.79

P = Phthalanilic acid.

The presence of polynuclear species could be ruled out on the basis of formation curves determined from the ligand metal ratio of 5 : 1 and 10 : 1 which were found to be identical. The highest value of $\bar{n} \approx 2$ (average number of ligands attached per metal ion) indicated the combining ratio of metal to ligand as 1 : 2. The formation constants were in the order

$$Mn^{II} < Co^{II} \leq Ni^{II} < Cu^{II} < Fe^{II}$$

The higher value of Fe^{II} complexes may be attributed to the higher value of CFSE of the metal ion in a strong ligand field. Such higher values are reported in the case of riboflavin, o-phenanthroline and folic acid[20]. Nitro group is a stronger σ and π electron acceptor and hence in the complexes of

4-nitrophthalanilic acids, the cation is less destabilised as compared to the proton. Methoxy group increases the electron density at the reaction centre and hence increases the stability of the chelate. A straight line obtained in between the values of log K_1 and ionisation potentials of the metal ions indicate that the formation of the first complex species is directly proportional to the ionisation potential of the central metal ion. Fe^{II} and Cu^{II} complexes were the exceptions which may be due to higher CFSE and Jahn-Teller effect, respectively.

The values of entropy changes are very high which may be due to the negative charge on the coordinating sites which brings about a shielding of central dipositive metal ion from exercising its orienting influence on the unfrozen distant water dipoles[21]. The electrostatic interaction also has a endothermic effect on the heats of reaction[22]. The contribution to the total change in enthalpy by metal-carboxylate bond is generally very small. The exothermic values given in each case are fairly high and can not be accounted by metal-oxygen bond only. This indicate the involvement of nitrogen atom in coordination.

References

1. W. F. Stack and H. A. Skinner, *Trans. Faraday Soc.*, 1967, **63**, 1136.
2. V. S. Sharma and H. B. Mathur, *Indian J. Chem.*, 1965, **3**, 475.
3. E. V. Raju and H. B. Mathur, *J. Inorg. Nucl. Chem.*, 1969, **31**, 425.
4. J. E. Letter, Jr. and J. E. Bauman, Jr., *J. Am. Chem. Soc.*, 1970, **92**, 437.
5. G. Beech, *Q. Rev. Chem.*, 1970, **23**, 410.
6. S. K. Srivastava, E. V. Raju and H. B. Mathur, *J. Inorg. Nucl. Chem.*, 1973, **35**, 258.
7. E. V. Raju and H. B. Mathur, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2181.
8. S. J. Ashcroft and C. J. Mortimer, "Thermochemistry of Transition Metal Complexes", Academic Press, New York, 1970.
9. C. L. Sharma and P. K. Jain, *J. Indian Chem. Soc.*, 1978, **55**, 892.
10. I. P. Saraswat, C. L. Sharma and A. Sharma, *J. Indian Chem. Soc.*, 1978, **55**, 757.
11. J. Kielland *J. Am. Chem. Soc.*, 1937, **59**, 1675.
12. "Technique of Organic Chemistry", ed. A. Weissberger and E. S. Proskauer, Interscience, New York, 1955, Vol. 8, p. 139.
13. N. V. Subba Rao and C. V. Ratnam, *J. Sci. Ind. Res.*, 1962, **47**, 218.
14. H. M. N. H. Irving and U. S. Mahnot, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1215.
15. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, **1954**, 2904.
16. J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions", P. Haase, Copenhagen, 1941.
17. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 1945, **67**, 2003.
18. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, **1953**, 3394.
19. L-G. Van Uitert and C. G. Haas, *J. Am. Chem. Soc.*, 1953, **75**, 451.
20. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192.
21. M. N. Evans and H. S. Frank, *J. Chem. Phys.*, 1945, **13**, 507.
22. G. Degischer and G. H. Mancollas, *J. Chem. Soc.* (*A*), 1970, 1125.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 680-682

Kinetics and Mechanism of Base Catalysed Hydrolysis of *m*-Methoxybenzoic Acid Hydrazide

M. H. JAGDALE, A. Y. NIMBALKAR, (Miss) J. D. MANE and (Miss) P. A. GIDDE

Department of Chemistry, Shivaji University, Kolhapur-416 004

Manuscript received 11 March 1983, revised 20 February 1984, accepted 3 May 1984

The kinetics and mechanism of base catalysed hydrolysis of *m*-methoxybenzoic acid hydrazide in aqueous sodium hydroxide over the range of 0.02-6.0 *M*, have been investigated spectrophotometrically at 70°. The reaction has been found to follow pseudo-first order rate law. The reaction leads to the formation of hydrazine and *m*-methoxybenzoic acid. Three cases of hydrolysis, applicable to three different ranges of NaOH concentrations were recognised. The activation parameters have been evaluated. The rate constants increase with increase in base concentration and attains optimum value at 3 *M*.

RECENTLY the kinetics of base catalysed hydrolysis of amides have been studied by a number of investigators[1]. Similar effects on the kinetics of alkaline hydrolysis of formhydrazide have been reported[2], but so far no kinetic study have been made on the base catalysed hydrolysis of aromatic hydrazides.

The hydrazides are expected to undergo hydrolysis catalysed by both acid and base. The acid catalysed hydrolysis of hydrazides have been reported[3,4,5]. This paper describes the studies of the kinetics and mechanism of the base catalysed hydrolysis of *m*-methoxybenzoic acid hydrazide in an attempt to see its similarity with formhydrazide hydrolysis[2].

Experimental

m-Methoxy benzhydrazide was prepared by a known method[6] and recrystallised from water, m.p. 94°. The alkaline solvents were made by diluting the fresh stock solution of NaOH (reagent grade).

All kinetic experiments were carried out in a thermostated water bath and reaction rates were determined spectrophotometrically. The rate constants were measured from the appearance of hydrazine[7] and the optical densities measured at 460 mμ on a SPEKOL.

Results and Discussion

The rate constants were found to increase with increase in the base concentration attaining maxima at 3.0 *M* and then decreased gradually (Table 1). This suggests change in mechanism after 3.0 *M* base concentration. Pseudo-first order rate constants in the hydrazide are independent of its change in concentration (Table 2).

Kinetics in dilute sodium hydroxide solutions: In the sodium hydroxide solution (< 3 *M*) *m*-CH_3O-$C_6H_4CONHNH_2$ molecule and OH^- ion combine to form complex (1) which decomposes slowly to form product (2).

TABLE 1—RATE CONSTANTS OF BASE CATALYSED HYDROLYSIS OF *m*-METHOXYBENZOIC ACID HYDRAZIDE AT 70°

NaOH *M*	k_{obs} $\times 10^3$ min^{-1}	NaOH *M*	k_{obs} $\times 10^3$ min^{-1}
0.02	0.498	0.6	3.78
0.04	0.681	0.7	3.86
0.05	0.712	0.8	4.09
0.06	0.899	0.9	5.05
0.08	1.020	1.0	6.31
0.10	1.490	1.5	6.38
0.20	2.240	2.0	8.96
0.30	2.670	3.0	9.41
0.40	2.880	4.0	9.04
0.50	3.280	5.0	8.63
		6.0	7.94

TABLE 2—EFFECT OF CHANGE OF SUBSTRATE CONCENTRATION ON HYDROLYSIS OF *m*-METHOXYBENZOIC ACID HYDRAZIDE SOLUTION AT 70°

Hydrazide $\times 10^{-4}$ *M*	NaOH *M*	k $\times 10^3$ min^{-1}
2.344	0.5	3.283
1.758	0.5	3.223
1.172	0.5	3.289

$$m\text{-}CH_3OC_6H_4CONHNH_2 + OH^- \rightleftharpoons m\text{-}CH_3O-C_6H_4-\underset{\displaystyle NHNH_2}{\overset{\displaystyle O^-}{\underset{|}{\overset{|}{C}}}}-OH \quad (1)$$

equil. constant K

$$m-CH_3O-C_6H_4-\underset{\displaystyle NHNH_2}{\overset{\displaystyle O^-}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow{\text{slow}} m-CH_3O-C_6H_4COO^- + NH_2-NH_2 \quad (2)$$

rate constant k

Rate laws and k are given by

$$-\frac{d(Hy)}{dt}=K\ (A^-) \quad (3)$$

$$-\frac{d(Hy)}{dt}=k_{obs}\ (Hy) \quad (4)$$

$$K=\frac{(A^-)}{(A)}\times\frac{\nu A^-}{\nu A\ a_{OH^-}} \quad (5)$$

where $A=m-CH_3O-C_6H_4CONHNH_2$,

$$A^-=m-CH_3O-C_6H_4-\underset{\displaystyle O^-}{\overset{\displaystyle OH}{C}}-NHNH_2,$$

Hy = total hydrazide $(A+A^-)$,
ν = activity coefficient, a = activity.

The overall rate constants k_{obs} is combined with K and k.

$$\frac{1}{k_{obs}}=\frac{1}{K}+\frac{1}{k\ K}\ \frac{\nu A^-}{\nu A\ a_{OH^-}} \quad (6)$$

A plot of $\frac{1}{k_{obs}}$ *vs.* $\frac{\nu A^-}{\nu A\ a_{OH^-}}$ gives a straight line with a slope $\frac{1}{k\ K}$ and intercept $\frac{1}{K}$ (Fig. 1). The values of a_{OH^-} were assumed to be equal to those of mean

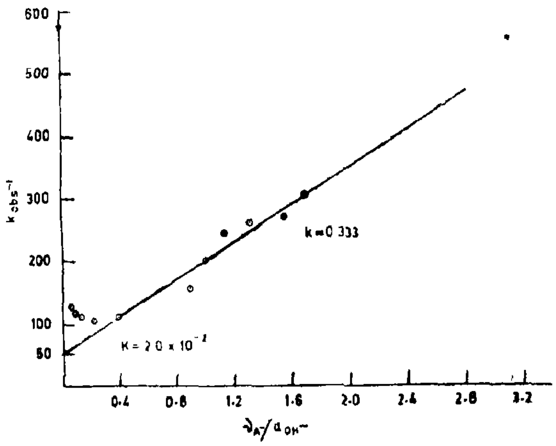


Fig. 1

activity (a ±) of NaOH calculated by using mean activity coefficient obtained by interpolation from the reported data[6]. The values of νA^- were calculated from the approximate Debye-Huckel equation.

$$\log \nu A^-=-0.510\ Z^2\ \frac{I^{1/2}}{(1+1.15\ I^{1/2})}$$

where Z is the valency of A^- (equal to unity) and I the ionic strength of aqueous NaOH solution.

A good extrapolation was obtained giving $K=2.0\times10^{-2}$ min^{-1} and using this value of K, the slope gives k=0.333. Consequently, the linear plot indicates that in the region of NaOH concentration lower than *ca.* 3.0 mole the reaction scheme is given by equations 1 and 2, the rate determining step being the unimolecular decomposition of the complex (Fig. 2).

Above *ca.* 3.0 mole, $\frac{1}{k_{obs}}$ decreases linearly with increasing [NaOH]. Thus, the base catalysed hydrolysis would proceed by equation (1) in these regions of NaOH, the changes of hydration number being disregarded[8].

Kinetics in moderately concentrated sodium hydroxide solutions : The reaction scheme for base catalysed hydrolysis of *m*-methoxybenzoic acid hydrazide in moderately concentrated NaOH solution is given by

$$m-CH_3O-C_6H_4CONHNH_2+OH^- \overset{slow}{\rightleftharpoons} CH_3OC_6H_4COO^-+NH_2-NH_2 \quad (7)$$

It is observed from the plot k_{obs} *vs.* OH^- that k_{obs} is nearly constant in the narrow range of [NaOH] *ca.* 3.0 *M* and further decreases linearly with increasing concentration of sodium hydroxide. Thus hydrolysis of *m*-methoxybenzoic acid hydrazide would proceed by equation (7), in these region of [NaOH], the change of hydration number being disregarded.

Correlation of k_{obs} with acidity function H : As suggested by Yagil and others[9], these results belong to the group containing reactions expected to give a linear plot of $\log k_{obs}$ *vs.* $H_-+\log C_{H_2O}$ with unit slope. This plot shown in Fig. 2 together with the Zucker-Hammett type plot $\log k_{obs}$ *vs.* H_- indicate

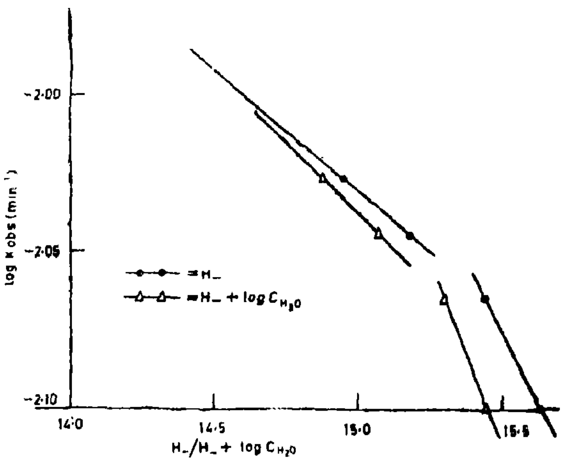


Fig. 2. Yagil plot for alkaline hydrolysis of *m*-methylbenzoic acid hydrazide at 70°.

that the two linear parts can be obtained with slope deviating greatly from unity with boundary points between them. As suggested by Rochester in equation (8),

$$\log k_{obs}-H_-={}'V'\ \log a_{H_2O}+\text{constant} \quad (8)$$

for the reactions in strongly basic media, 'V' parameter is evaluated.

The parameter 'V' in the above equation is the slope of the plot of $\log k_{obs}-H_-$ *vs.* $\log a_{H_2O}$ (Fig. 3). These parts correspond to two types of hydrolysis mechanism.

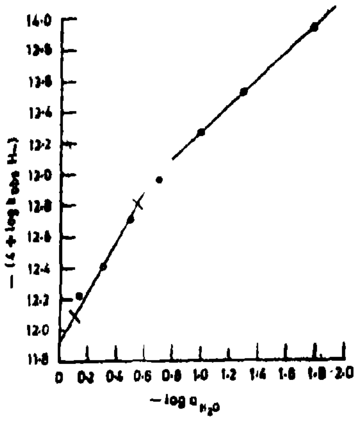


Fig. 2

References

1. R. H. DEWOLFE and R. C. NEWCOMB, *J. Org. Chem.*, 1971, **36**, 3870.
2. M. MASHIMA and F. IKEDA, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1371.
3. M. H. JAGDALE and A. Y. NIMBALKAR, *J. Indian Chem. Soc.*, 1973, **50**, 788.
4. M. H. JAGDALE and A. Y. NIMBALKAR, *J. Shivaji Univ. (Science)*, 1975, **15**, 41.
5. M. H. JAGDALE and A. Y. NIMBALKAR, *Acta Ciencia Indica*, 1976, **2**, 336.
6. P. A. S. SMITH, "Organic Reactions", ed. ROGER ADAM, John Wiley, New York, 1946, p. 367.
7. W. W. GEORGE and J. D. CHRISP, *Anal. Chem.*, 1952, 24, 2006.
8. G. AKERLOF and G. KEGELES, *J. Chem. Soc.*, 1940, 62 620.
9. M. AUBAR, M. BOSTELSKY, D. SAMUEL and G. YAGIL, *J. Am. Chem. Soc.*, 1963, **85**, 2380.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 683-686

Cation Exchange Separation of Metal Ions in Aqueous Sodium Glycollate Media

M. SITA RAMA REDDY, ANIMESH K. GHOSE*

Chemical Laboratories, University of Allahabad, Allahabad-211 002

and

LALIT C. T. EUSEBIUS

Department of Chemistry, Ewing Christian College, Allahabad-211 003

Manuscript received 15 March 1983, revised 13 December 1983, accepted 21 July 1984

The cation exchange behaviour of 20 cations has been studied on strongly acidic Amberlite IR-120 (20-50 mesh, 8-10% cross linkage, Na^+ form) in aqueous sodium glycollate media. The distribution coefficients (*K*) determined through batch technique revealed the possibilities of a number of separations. The actual separations of metal ions were obtained on a short resin column of ~7.5 cm height. The ternary separations were also achieved on ~10 cm long resin column.

The distribution coefficients (*K*), column elution behaviour, elution curves and results of some of the binary and ternary cation mixtures along with standard deviations are presented.

THE use of complexing agents has tremendously increased the application of ion-exchange chromatography. For obtaining a specific separation the ion-exchange equilibria can suitably be adjusted with the help of complexants. Sodium glycollate has pronounced complexation tendency and many metal glycollates are known[1-3]. A systematic cation exchange study of metal ions in α-hydroxyisobutyric acid with alcohols was reported[4]. No information is available on the use of sodium glycollate in the ion-exchange chromatography. Therefore, the present investigation was undertaken to study the distribution coefficients of a number of metal ions in 0.04-0.40 mol dm^{-3} aqueous sodium glycollate, the elution behaviour, and the results of resolution of synthetic binary and ternary mixtures along with standard deviations are presented in this paper.

Experimental

Materials: Purified strongly acidic cation exchanger Amberlite IR-120 (20-50 mesh, 8-10% cross-linked, Na^+ form) was used for both batch and column studies. The resin capacity and its water contents were ~2.85 meq/g and ~35%, respectively.

Fresh 0.05 to 0.20 mol dm^{-3} solutions of Mg^{II}, Al^{III}, Ca^{II}, Cr^{III}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Sr^{II}, Cd^{II}, Ba^{II}, La^{III}, Ce^{III}, Pb^{II} and Th^{IV} were prepared from their reagent grade nitrate (AnalaR or Johnson Mathey). Fe^{III}, Ga^{III}, In^{III} and Hg^{II} solutions were prepared directly in sodium glycollate solution from their nitrate. Aqueous 1.0 mol dm^{-3} solution of sodium glycollate (Fluka AG Buchs SG) was used. Wash solutions were 0.04-0.20 mol dm^{-3} aqueous sodium glycollate as the case may be.

Procedure:

Distribution coefficients (K): The batch technique was employed for the determination of distribution coefficients. Air dried resin (1 g) was added to a constant amount of metal ion and varying amounts (0.04 to 0.40 mol dm^{-3}) of sodium glycollate solution. The overall volume was kept at 25 cm^3. The solutions were mechanically shaken in wrist motion microid flask shakers (Griffin & George Co.) for 1 h and then filtered to separate the resin. The metal ion content were determined complexometrically[5-8] in the solution phase. The distribution coefficient (*K*) was determined by using the relationship, K = mg metal ion per g resin/mg metal ion per cm^3 solution.

All experiments were conducted in duplicate at 30±2°. The values of *K* are presented in Table 1. The experimental error was found to be less than ± 5%.

Column chromatographic studies: The following method was used for the resolution of binary and ternary mixtures. Fully water swollen resin slurry (~5 g) was transferred to the graduated chromatographic column to a height of ~7.5 cm. It was washed with various washing solutions as the case may be. The 25 cm^3 of the feed containing metal ions to be separated, was prepared in duplicate in 0.04/0.12/0.20 mol dm^{-3} aqueous sodium glycollate solution. The feed was passed through the preconditioned column at a flow rate of 1.0±0.3 cm^3 min^{-1}. The effluent was collected from the beginning of sorption step unless otherwise mentioned. The most weakly sorbed metal ions often followed the effluent and were quantitatively recovered with 0.04-0.20 mol dm^{-3} sodium glycollate eluent. The

TABLE 1—DISTRIBUTION COEFFICIENTS (K) IN AQUEOUS SODIUM GLYCOLLATE

Metal ion	Distribution coefficient (K) Concentration of sodium glycollate, mol dm^{-3}				
	0.04	0.12	0.20	0.28	0.40
Mg^{II}	475	144	41	82	14
Al^{III}	110	12	10	2	1
Ca^{II}	475	145	41	32	15
Cr^{III}	75	18	8	1	1
Mn^{II}	475	113	37	20	9
Fe^{III}	37	4	3	2	1
Co^{II}	193	37	11	2	1
Ni^{II}	212	34	11	6	1
Cu^{II}	75	8	5	1	1
Zn^{II}	10^4	30	8	2	1
Ga^{III}	45	6	4	2	1
Sr^{II}	10^4	141	100	58	37
Cd^{II}	465	56	15	3	1
In^{III}	325	8	6	4	1
Ba^{II}	10^4	475	225	167	114
La^{III}	10^4	275	58	17	3
Ce^{III}	10^4	151	22	11	1
Hg^{II}	3	2	1	1	1
Pb^{II}	475	75	30	13	6
Th^{IV}	141	17	8	3	1

strongly sorbed metal ions were either desorbed with higher concentrations of sodium glycollate solutions or with any other suitable eluent.

Results and Discussion

The distribution coefficient values presented in Table 1 show that the affinity of almost all metal ions decrease with increase of concentration of sodium glycollate. This decrease of K values is due to the complexation of metal ions with glycollate resulting in the formation of either neutral or low positively charged metal-ligand species. As the concentration of glycollate ion is further increased the number of neutral or low positively charged species also increases thereby causing further decrease in the K values. The very low K values of Hg^{II} from 0.04 to 0.40 mol dm^{-3} suggest the formation of either large number of neutral species having very low dissociation or negatively charged species.

Prediction of separation possibilities : The very low K values (~ 3) of Hg^{II} at 0.04 mol dm^{-3} sodium glycollate indicate its separation from all other metal ions. Hg^{II} follows the effluent and therefore, effluent is collected from the beginning of the sorption step. It can easily be quantitatively recovered with 0.04 mol dm^{-3} sodium glycollate eluent while the other strongly sorbed metal ions may be eluted either with 0.40 mol dm^{-3} sodium glycollate or with mineral acids.

At 0.12 mol dm^{-3} sodium glycollate the K values of Fe^{III}, Cu^{II}, Ga^{III} and In^{III} are sufficiently low to allow their separation from Mg^{II}, Co^{II}, Mn^{II}, Sr^{II}, Cd^{II}, Ba^{II}, La^{III}, Ce^{III} and Pb^{II} metal ions having sufficiently high K values. Fe^{III}, Cu^{II}, Ga^{III} and In^{III} can be recovered first with 0.12 mol dm^{-3} sodium glycollate eluent followed by elution of other strongly retained metal ions either with 0.40 mol dm^{-3} sodium glycollate or mineral acids.

Th^{IV} has K value 8 at 0.20 mol dm^{-3} sodium glycollate medium and can be separated from other metal ions Mn^{II}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, La^{III} and Ce^{III} having sufficiently high K values to be retained onto the resin bed. Sr^{II} and Ba^{II} can be separated from other metal ions in 0.40 mol dm^{-3} sodium glycollate medium. Sr^{II} and Ba^{II} are strongly sorbed due to high K values whereas other metal ions sorbed weakly and therefore, can be eluted with 0.40 mol dm^{-3} sodium glycollate eluent.

On the basis of possibilities of various binary separations a number of ternary separations are also predicted. All the binary and ternary separations thus predicted are presented in Table 2.

Separation on column : A large number of binary and ternary separations were achieved through column chromatography but a few separations are being discussed here.

Binary separations : Hg^{II} from all other metal ions was separated with feed prepared in 0.04 mol dm^{-3} aqueous sodium glycollate. Hg^{II} was detected even in the effluent and therefore, the effluent was collected, in 5 ml fractions, from the beginning of sorption step. The whole of Hg^{II} was recovered with $\sim$60 cm^3 of 0.04 mol dm^{-3} sodium glycollate as eluent. The strongly retained metal ions were desorbed with 0.40 mol dm^{-3} sodium glycollate solution except Mg^{II}, Ca^{II}, Sr^{II} and Ba^{II} which were

TABLE 2—POSSIBLE BINARY AND TERNARY SEPARATIONS OF METAL IONS IN AQUEOUS SODIUM GLYCOLLATE MEDIA

Binary Separation

Sl. no.	First component eluted	Second component eluted
1.	Hg^{II}	All other metal ions
2.	Fe^{III}, Cu^{II}, Ga^{III}, In^{III}	Mn^{II}, Cd^{II}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, La^{III}, Ce^{III}, Pb^{II}
3.	Al^{III}, Th^{IV}	Mn^{II}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, La^{III}, Ce^{III}, Pb^{II}
4.	Th^{IV}	Mn^{II}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, La^{III}, Ce^{III}, Pb^{II}
5.	Al^{III}, Cr^{III}, Zn^{II}	Sr^{II}, Ba^{II}, Pb^{II}
6.	Co^{II}, Ni^{II}, Cd^{II}	Sr^{II}, Ba^{II}, La^{III}
7.	Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}	Al^{III}, Cr^{III}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Ga^{III}, In^{III}, Cd^{II}, Hg^{II}, Th^{IV}
8.	Mn^{II}, La^{III}, Ce^{III}, Pb^{II}	Sr^{II}, Pb^{II}
9.	Mg^{II}, Ca^{II}	Ba^{II}
10.	Sr^{II}, Ba^{II}	Other metal ions

(Table 2 contd.)

Ternary Separation

	First component eluted	Second component eluted	Third component eluted
1.	Hg^{II}	Fe^{III}, Cu^{II}, Ga^{III}, In^{III}	Mn^{II}, Cd^{II}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, La^{III}, Ce^{III}, Pb^{II}
2.	Hg^{II}	Th^{IV}	Mn^{II}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, La^{III}, Ce^{III}
3.	Hg^{II}	Al^{III}, Cr^{III}, Zn^{II}	Sr^{II}, Ba^{II}, La^{III}, Ce^{III}
4.	Fe^{III}, Cu^{II}, Ga^{III}, In^{III}	Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, La^{III}, Ce^{III}, Pb^{II}	Sr^{II}, Ba^{II}
5.	Al^{III}, Cr^{III}	Mg^{II}, Cd^{II}, Mn^{II}, La^{III}, Ce^{III}, Pb^{II}	Sr^{II}, Ba^{II}
6.	Th^{IV}	Ca^{II}, Mg^{II}, La^{III}, Ce^{III}, Pb^{II}	Sr^{II}, Ba^{II}
7.	Ga^{III}, In^{III}, Fe^{III}, Cu^{II}	Ni^{II}, Co^{II}	Ca^{II}, Sr^{II}, Ba^{II}, La^{III}, Ce^{III}

eluted with 4.0 mol dm^{-3} HCl. The results of separations are reported in Table 4.

$Fe^{III}/Cu^{II}/Ga^{III}$ or In^{III} from Mn^{II}, Cd^{II}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, Pb^{II}, La^{III} or Ce^{III} separation feed was prepared in 0.12 mol dm^{-3} sodium glycollate solution. Fe^{III}, Cu^{II}, Ga^{III} or In^{III} were recovered first quantitatively with 0.12 mol dm^{-3} sodium glycollate eluent. The elution characteristics of these metal ions are presented in Table 3. Then the strongly retained metal ions were eluted with either 0.40 mol dm^{-3} sodium glycollate or with mineral acid. The results of separation along with standard deviations are presented in Table 4.

TABLE 3—ELUTION CHARACTERISTICS OF METAL IONS ON AMBERLITE IR-120 IN SODIUM GLYCOLLATE

Metal ion	BTV cm^3	VEP cm^3	TEV cm^3	Eluent (Na-glycollate) mol dm^{-3}
Hg^{II}	5	30	60	0.04
Ga^{III}	0	30	40	0.12
In^{III}	10	40	70	0.12
Fe^{III}	5	30	40	0.12
Cu^{II}	5	30	90	0.12
Ni^{II}	0	50	110	0.20
Co^{II}	25	130	220	0.20
Cd^{II}	45	155	245	0.20
Zn^{II}	15	75	125	0.20
Al^{III}	40	60	90	0.20
Cr^{III}	10	40	90	0.20
Th^{IV}	25	45	95	0.20
Ce^{III}	40	100	120	0.20
La^{III}	0	30	60	0.40
Mn^{II}	0	60	110	0.40
Pb^{II}	10	50	90	0.40
Ce^{III}	0	25	50	0.40

TABLE 4—RESULTS OF RESOLUTION OF BINARY MIXTURES

Metal ions	Taken: Mean amount mg	Found: Mean amount mg	Number of determinations	Standard deviation	Eluent
1st. constituent eluted					
Hg^{II}	106.58	105.25	36	±0.20	A
Fe^{III}	24.57	24.60	18	±0.12	B
Cu^{II}	33.52	33.70	18	±0.14	B
Ga^{III}	28.18	28.00	18	±0.12	B
In^{III}	25.47	25.25	18	±0.04	B
Th^{IV}	80.62	80.20	16	±0.06	C
2nd. constituent eluted					
Mg^{II}	11.80	11.92	12	±0.14	D
Al^{III}	9.35	9.15	02	±0.10	E
Ca^{II}	20.25	20.20	12	±0.06	D
Cr^{III}	15.38	15.48	02	±0.05	E
Mn^{II}	31.28	31.40	12	±0.11	E
Fe^{III}	21.05	21.20	02	±0.12	E
Co^{II}	30.82	30.60	02	±0.09	E
Ni^{II}	31.68	31.50	02	±0.10	E
Cu^{II}	33.52	33.70	02	±0.12	E
Zn^{II}	31.28	31.10	02	±0.12	E
Ga^{III}	22.13	22.00	02	±0.08	E
Sr^{II}	43.00	42.80	12	±0.15	D
Cd^{II}	52.24	52.00	10	±0.20	E
In^{III}	26.65	26.85	02	±0.16	E
Ba^{II}	65.15	65.40	12	±0.22	D
La^{III}	48.06	48.26	12	±0.16	E
Ce^{III}	35.72	35.98	12	±0.12	E
Pb^{II}	102.12	102.92	12	±0.30	E
Th^{IV}	82.32	82.62	02	±0.22	E

A = 0.04 mol dm^{-3} Na-glycollate.
B = 0.12 mol dm^{-3} Na-glycollate.
C = 0.20 mol dm^{-3} Na-glycollate.
D = 0.40 mol dm^{-3} Na-glycollate.
E = 4.00 mol dm^{-3} HCl.

Th^{IV} from Mn^{II}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, Pb^{II}, La^{III} or Ce^{III} was separated from 0.20 mol dm^{-3} sodium glycollate solution. Th^{IV} was first eluted with 0.20 mol dm^{-3} sodium glycollate eluent. The breakthrough of Th^{IV} was at 25 cm^3 and the total elution volume ~95 cm^3. The strongly sorbed other metal ions were subsequently stripped off as described earlier. The results of these separations with standard deviations are presented in Table 4. Fig. 1 shows elution curve for the separation of Th^{IV} from La^{III}.

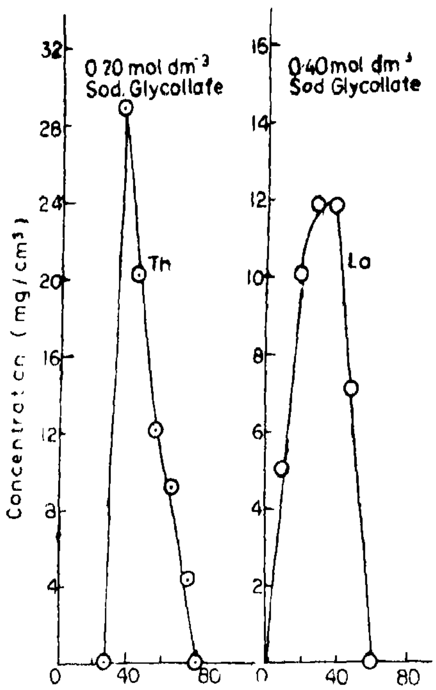


Fig. 1. Elution curve for Th^{IV}-La^{III}.

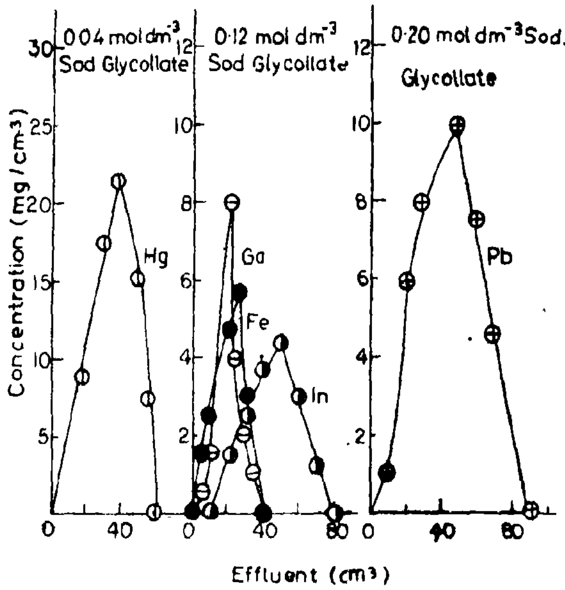


Fig. 2. Elution curve for Hg^{II}-Fe^{III}/In^{III}/Ga^{III}-Pb^{II}.

Ternary separations: For resolving ternary mixtures the height of the resin bed was increased to ~10 cm.

Hg^{II}-Fe^{III}/Cu^{II}/Ga^{III}/In^{III}-Mn^{II}/Cd^{II}/Mg^{II}/Ca^{II}/Sr^{II}/Ba^{II}/Pb^{II}/La^{III}/Ce^{III} metal ions feed was prepared in 0.04 mol dm^{-3} sodium glycollate by mixing any three of the metal ions to be separated and passed through preconditioned resin column. Firstly, Hg^{II} was recovered quantitatively with ~60 cm^3 of 0.04 mol dm^{-3} sodium glycollate followed by desorption of not too strongly sorbed metal ions Fe^{III}, Cu^{II}, Ga^{III} or In^{III} with 0.12 mol dm^{-3} sodium glycollate solution. Finally, strongly retained third constituent metal ion was eluted as follows: Cd^{II}, La^{III} or Ce^{III} with ~60 cm^3, Pb^{II} with ~90 cm^3, and Mn^{II} with ~110 cm^3 of 0.40 mol dm^{-3} sodium glycollate eluent; Mg^{II}, Ca^{II}, Sr^{II} or Ba^{II} were eluted with 4.0 mol dm^{-3} HCl. Fig. 2 shows resolution of Hg^{II}-Fe^{III}/In^{III}/Ga^{III}-Pb^{II} ternary mixtures.

Fe^{III}/Cu^{II}/Ga^{III}/In^{III}-Mn^{II}/Co^{II}/Ni^{II}/Zn^{II}/Cd^{II}/Pb^{II}/La^{III}/Ce^{III}-Sr^{II}/Ba^{II} metal ions feed was prepared in 0.12 mol dm^{-3} sodium glycollate solution. Fe^{III}, Cu^{II}, Ga^{III} or In^{III} followed the feed effluent and were quantitatively eluted with 0.12 mol dm^{-3} sodium glycollate as described earlier. Mn^{II}/Co^{II}/Ni^{II}/Zn^{II}/Cd^{II}/Pb^{II}/La^{III}/Ce^{III} were then eluted with 0.40 mol dm^{-3} sodium glycollate followed by the elution of very strongly sorbed Sr^{II} or Ba^{II} with 4.0 mol dm^{-3} HCl as described earlier.

Th^{IV}-Mg^{II}/Ca^{II}/Pb^{II}/La^{III}/Ce^{III}-Sr^{II}/Ba^{II} metal ions feed was prepared in 0.20 mol dm^{-3} sodium glycollate solution. Firstly, Th^{IV} was quantitatively eluted with ~100 cm^3 of 0.20 mol dm^{-3} sodium glycollate followed by the elution of Mg^{II}/Ca^{II}/Pb^{II}/La^{III}/Ce^{III} with 0.40 mol dm^{-3} sodium glycollate as described earlier. Finally, Sr^{II}/Ba^{II} was eluted with 4.0 mol dm^{-3} HCl.

Thus aqueous sodium glycollate can effectively be employed for the separations of a large number of metal ions. The column kinetics and other parameters required for achieving separations were found to be favourable.

Acknowledgement

The authors are thankful to the U.G.C., New Delhi, for the award of a fellowship (M.S.R.R.).

References

1. S. Ahrland, *Acta Chem. Scand.*, 1953, **7**, 485.
2. T. Moeller, "Inorganic Chemistry", Asia Publishing House, New Delhi, 1966.
3. A. Sonesson, *Acta Chem. Scand.*, 1958, **12**, 165.
4. J. Alexa, *Collect. Czech. Chem. Commun.*, 1965, **30**, 2344.
5. H. A. Flaschka, "EDTA Titrations", Pergamon Press, Oxford, 1964.
6. R. Ghose, A. Mahan and A. K. Dey, *Indian J. Chem., Sect. A*, 1976, **14**, 518.
7. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", 3rd Ed., Longmans, London, 1961.
8. F. J. Welcher, "The Analytical Uses of EDTA", Van Nostrand, New York, 1967.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 687-689

The Solubility and Micellar Behaviour of dl-tris(en) Cobalt(III) Soaps in Various Solvents

WAHID U. MALIK, AJAY K. JAIN*, V. K. VELU and A. K. CHHIBBAR

Department of Chemistry, University of Roorkee, Roorkee-247 667

Manuscript received 20 January 1984, accepted 21 July 1984

A new series of cobalt complex soaps, *viz.* dl-tris(en) cobalt(III) myristate, palmitate and stearate have been synthesised and their solubility behaviour in various solvents was investigated using ^{60}Co as tracer. The results indicate that these cobalt complex soaps are about 10-50 times more soluble than ordinary cobalt soaps. The higher solubility has been explained on the basis of weaker polar bonding. Further, the solubility has been found to increase as the length of the hydrocarbon chain in the soap decreases. The variation in the solubility of these soaps with temperature has been used to determine their critical micelle concentration and Krafft point.

PLIPEL[1], while reviewing the properties of organic solutions of heavy metal soaps, has pointed out that they are soluble in a vide variety of organic solvents and yield gels, colloidal dispersions and liquids. However, our investigations during the last fifteen years using highly sensitive radiotracer technique have shown that cobalt[2,3], cadmium[4], silver[5] and chromium[5] soaps are only sparingly soluble in most of the organic solvents at room temperature. The low solubility of metal soaps adversely affect their utility in industry. For example, it is reported that difficulties are encountered in making appropriate and specific lubricating preparations[6] due to the low solubility of the metal soaps. It is thus expected that these soaps can be more profitably used if their solubility can be enhanced. We have, therefore, started preparing modified metal soaps by interacting metal complex cations with ionic surfactants and have found that cobalt hexammine soaps[7,8] are much more soluble than cobalt soaps. This increase in solubility has been assigned to large size[7] of cobalt hexammine cation. In order to further support this conclusion, we have synthesized dl-tris(en) cobalt(III) soaps and report in the present communication on their solubility and micellization behaviour in large number of pure solvents.

Experimental

Sodium myristate, palmitate and stearate (reagent grade BDH) were used after purification by extraction using acetone and then recrystallisation from alcohol. All other reagents were of AR grade and solvents purified by standard methods. The radiotracer ^{60}Co was obtained as cobalt chloride in HCl solution from B.A.R.C., Bombay.

Preparation of labelled dl-tris(en) cobalt(III) chloride : A small amount of ^{60}Co activity was added to an aqueous solution of 2.4 g inactive cobalt chloride in 10 ml water and the resulting mixture was warmed up to bring about complete isotopic exchange. This solution was then used for the preparation of labelled dl-tris(en) cobalt(III) chloride by the reported method[9].

Preparation of labelled dl-tris(en) cobalt(III) soaps : Labelled dl-tris(en) cobalt(III) myristate, palmitate and stearate were prepared by interacting aqueous solution of the corresponding sodium soaps (0.01 *M*) with an aqueous solution of labelled dl-tris(en) Co^{III} chloride (0.02 *M*). The complex was added in slight excess. The precipitated soaps were filtered, washed with double-distilled water and alcohol and then dried in a vacuum desiccator. The unlabelled cobalt complex soaps were similarly prepared and the formulae were assigned on the basis of elemental analysis (Table 1).

TABLE—1

Soaps	Analysis % ; Found/(Calcd.)		
	C	H	N
dl-tris(en) Co^{III} stearate $Co(en)_3(C_{17}H_{35}COO)_3$	66.43 (66.14)	11.76 (11.99)	7.58 (7.91)
dl-tris(en) Co^{III} palmitate $Co(en)_3(C_{15}H_{31}COO)_3$	64.75 (64.50)	12.08 (11.78)	8.10 (8.86)
dl-tris(en) Co^{III} myristate $Co(en)_3(C_{13}H_{27}COO)_3$	62.92 (62.57)	11.65 (11.49)	9.40 (9.12)

Solubility measurements : Each saturated solution was prepared by the agitation of an excess of labelled cobalt complex soap in a pyrex stoppered conical flask about half-full of solvent. Attainment of solubility equilibria was indicated by the constancy of the counting rate (activity) on successive measurements with supernatant solution. Aliquots were filtered through Whatman 42 paper and their activity determined on a gamma ray scintillation spectrometer. Specific activity of each cobalt complex soap was determined by measuring the activity of the standard solution of the soap in methanol. All activity measurements were made

TABLE 2—SOLUBILITY VALUES OF DL-TRIS(en) COBALT(III) SOAPS AT 30°

Solvent	dl-tris(en) Co^{III} myristate $\times 10^{-5}$ M	dl-tris(en) Co^{III} palmitate $\times 10^{-5}$ M	dl-tris(en) Co^{III} stearate $\times 10^{-5}$ M	Hexammine Co^{III} stearate* $\times 10^{-5}$ M	Co^{II} stearate** $\times 10^{-5}$ M
Benzene	21.9	15.4	11.9	7.8	0.79
Toluene	41.0	26.7	17.9	8.1	0.84
m-Xylene	49.0	36.0	28.2	12.0	1.07
Nitrobenzene	18.5	15.8	11.5	7.0	0.88
Chlorobenzene	24.8	19.2	17.6	10.1	0.88
Ethyl methyl ketone	16.5	18.7	11.7	6.1	1.18
Water	6.0	6.0	5.2	4.8	0.42
Dioxan	25.0	21.5	18.2	15.7	1.08
Acetone	12.8	8.8	7.8	5.8	0.28

* Ref. 7. ** Ref. 3.

TABLE 3 C.S.T. AND CMC VALUES OF dl-TRIS(en) COBALT(III) SOAPS IN VARIOUS SOLVENTS

Solvent	Stearate		Palmitate		Myristate	
	C.S.T. °C	cmc $\times 10^{5}$ M	C.S.T. °C	cmc $\times 10^{5}$ M	C.S.T.	cmc $\times 10^{5}$ M
Benzene	51.5	36.0	47.5	44.0	44.0	61.0
Toluene	52.5	28.5	48.0	37.0	45.0	53.0
m-Xylene	58.0	43.0	50.0	59.0	46.0	77.0
Nitrobenzene	68.0	16.0	64.5	24.5	61.0	33.0
Chlorobenzene	63.0	18.5	59.0	22.0	57.0	34.0

under the same geometrical conditions and appropriate corrections were made for coincidence loss and the decay of the isotope.

Results and Discussion

Solubility behaviour : The solubility values of dl-tris(en) Co^{III} soaps (together with cobalt stearate[8] and hexammine cobalt stearate[7] for the purpose of comparison) are given in Table 2. It is seen that these cobalt complex soaps are not highly soluble in both the polar and non-polar solvents. However, they are about 10-50 times more soluble than the ordinary cobalt soaps[8]. This difference appears due to varying extent of polar bonding in the soaps. In ordinary cobalt soaps, carboxylate group which is a moderately strong base[10] interacts with cobalt(II) ion, a strong Lewis acid. Due to small size of Cu^{II} ion, strong polar bonding exists in the cobalt(II) soaps molecules leading to their low solubility both in polar and non-polar solvents[10]. On the other hand, the polar bonding becomes relatively weaker in dl-tris(en) Co^{III} soaps due to the larger size of the cation. This would naturally result in enhanced solubility of cobalt complex soaps in comparison to cobalt soaps in different solvents. This comparison suffers from a drawback that the hydrophobic content in cobalt(II) soap is different from that of dl-tris(en) cobalt(III) soaps which might be playing some role. However, the comparison of the solubility of dl-tris(en) Co^{III} stearate with that of hexammine Co^{III} stearate[7], both having the same hydrophobic content shows that the former has higher solubility than the latter one. This is evidently due to the weaker polar bonding in view of large size of $Co(en)_3^{3+}$ as compared to $Co(NH_3)_6^{3+}$ ion. Thus our results indicate that the metal soaps having large cationic part would have higher solubility due to weaker polar bonding.

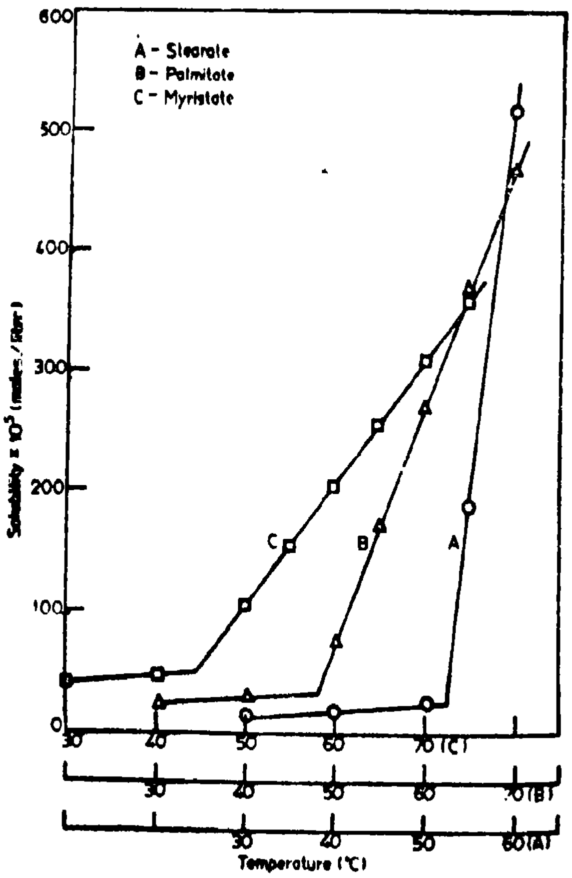


Fig. 1. Effect of temperature on the solubility of dl-tris (en) cobalt(III) soaps in toluene.

Effect of carbon chain length : It is further evident from Table 2 that the solubility of cobalt complex soaps is a function of carbon chain length and increases from stearate to myristate (molar volume decreasing). This observation is consistent with Hidlebrand and Scott's regular solution theory[11,12], that the solubility of a solute should increase with decrease of molar volume.

Effect of temperature on solubility : The effect of temperature on the solubility of cobalt complex soaps in benzene, toluene, *m*-xylene, nitrobenzene and chlorobenzene has also been investigated and the results obtained are shown only for toluene in Fig. 1. Similar results were obtained in other solvents. It is seen from Fig. 1 that at low temperature the variation in the solubility is rather small but after a particular temperature, known as critical solution temperature (C.S.T.) or Krafft point, the solubility is enhanced enormously with increase in temperature. This type of behaviour is characteristic of micelle forming substances and is evidently due to low solubility of the soap monomer and high solubility of the micelles. Such solubility behaviour was observed for cadmium[4], silver[5], chromium[8], cobalt[8] and hexammine cobalt(III)[7], lead[13], zinc[13,14] and copper[15-17] soaps. The solubility at C.S.T. is taken as critical micelle concentration (cmc) of the soap. The C.S.T. and cmc values so determined are given in Table 3. It is interesting to note that the C.S.T. value decreases and cmc value increases as the carbon chain length is shortened, whereas the solubility increases from stearate to myristate (Table 2). It may, therefore, be concluded that higher the solubility of the soap, the lower is its C.S.T. and higher the cmc. This relationship between solubility and cmc is of course expected because higher solubility indicates more affinity of the solvent for the soap monomer and thus leading to micellization at higher concentration.

Acknowledgement

One of the authors (V.K.V.) is thankful to the C.S.I.R., New Delhi for the award of a Junior Research Fellowship.

References

1. N. PILPEL, *Chem. Rev.*, 1963, **63**, 221.
2. W. U. MALIK, B. P. SINGH and A. K. JAIN, *Experientia*, 1967, **23**, 346.
3. W. U. MALIK, A. K. JAIN and M. J. SIDDIQUI, *Indian J. Chem., Sect. A*, 1976, **14**, 906.
4. W. U. MALIK and A. K. JAIN, *J. Colloid Interface Sci.*, 1969, **31**, 460.
5. W. U. MALIK, A. K. JAIN and O. P. JHAMB, *J. Chem. Soc. A*, 1971, 1514.
6. N. PILPEL, *Chem. Rev.*, 1966, **66**, 29.
7. W. U. MALIK, A. K. JAIN and M. J. SIDDIQUI, International Conference on Colloid and Surface Sci., Budapest, 1975, p 501.
8. A. K. JAIN, M. J. SIDDIQUI and R. P. B. SINGH, *J. Chem. Tech. Biotechnol.*, 1979, **29**, 499.
9. G. G. SCHLESSINGER, "Inorganic Laboratory Preparation", Chemical Publishing Co., New York, 1962.
10. M. P. FOWKES, "Solvent Properties of Surfactant Solutions", ed. K. J. SHINODA, Marcel Dekker, New York, 1967, Vol. 2, p. 81.
11. J. H. HILDEBRAND and R. L. SCOTT, "The Solubility of Non Electrolytes", Reinhold, New York, 1950.
12. J. H. HILDEBRAND and R. L. SCOTT, "Regular Solutions", Prentice-Hall, Englewood Cliffs, N. J., 1962.
13. R. L. LITTLE, *J. Colloid Interface Sci.*, 1966, **21**, 266.
14. E. R. MARTIN and R. C. PINK, *J. Chem. Soc.*, **1948**, **1750**.
15. S. M. NELSON and R. C. PINK, *J. Chem. Soc.*, 1954, **4412**.
16. S. M. NELSON and R. C. PINK, *J. Chem. Soc.*, 1952, 1744.
17. YAMURA TAKESHI, *Chem. Lett.*, 1977, 773.

J. Indian Chem. Soc.,
Vol. LXI, August 1984, pp. 690-693

Synthesis and Antimalarial Activity of Some New Quinazoline Derivatives

(MISS) N. SINGHAL, I. S. GUPTA and P. C. BANSAL

Department of Chemical Engineering and Technology, Panjab University, Chandigarh-160 014

Manuscript received 8 April 1982, revised 18 April 1984, accepted 21 July 1984

Dialkylaminoalkylamino and dialkylaminomethylarylamino derivatives of quinazoline have been synthesised for their antimalarial activity.

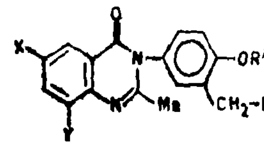
QUINAZOLINE is 5 : 6-benzopyrimidine. Pyrimidine derivatives including those with condensed ring systems occupy a very important place in the metabolism of plants, animals and microorganisms. The fusion of a benzene ring to a heterocyclic system, as for example in quinazoline, offers certain more advantages: (a) the benzene ring can be suitably substituted in four positions in quinazoline and such substitutions in a variety of cases can bring about valuable changes from the point of view of therapeutic activity, *e.g.* presence of OCH_3 group in quinine and atebrin, Cl in atebrin and chloroquine, $2NH_2$ groups in proflavin and $2CH_3$ groups in antrypol (germanin) is very important, (b) replacement of a heterocyclic ring by benzene is important from the point of view of essential metabolite-antimetabolite relationship, *e.g.* adenine is an essential metabolite whereas benzimidazole is its antimetabolite.

A heterocyclic ring like quinoline or acridine attached with a dialkylaminoalkylamino and dialkylaminomethylamino chain as in chloroquine[1-3], atebrine[4] and camoquine[5] is conducive to good antimalarial activity. Isofebrifugine and febrifugine, the alkaloids containing quinazoline ring system, isolated from *Dichroa febrifuga* Lour, show antimalarial activity against *P. gallinaceum*[6]. In the present communication, synthesis of some new quinazoline derivatives of general structures **I** and **II** and antimalarial activity of some of these compounds have been reported.

The compounds were synthesised by known procedures by condensing[7] substituted 3 : 1 : 4-benzoxazones[8] with appropriate amines[9]. The halogenated anthranilic acids were prepared by the reported method[10].

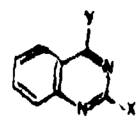
Two compounds, namely, 2-*p*-chloroanilino-4-(3'-*N*-diethylaminomethyl-4'-methoxy) quinazoline dihydrochloride (**IIm**) and 2-*p*-chloroanilino-4-(3'-N-diethylaminomethyl-4'-ethoxy) quinazoline dihydrochloride (**IIq**) were tested for antimalarial activity against *P. gallinaceum* in chicks (Table 1) at National Institute of Communicable Diseases, Delhi.

The following three compounds were sent to J. N. Medical College, Aligarh for the evaluation

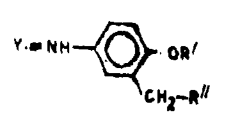


I

a, X = Y = H, R' = Et, R'' = NEt_2
b, X = Y = H, R' = Et, R'' = NMe_2
c, X = Y = H, R' = Et, R'' = $N(CH_2)_5$
d, X = Y = H, R = Me, R'' = NEt_2
e, X = Y = H, R' = Me, R'' = NMe_2
f, X = Y = H, R' = Me, R'' = $N(CH_2)_5$
g, X = Cl, Y = H, R' = Et, R'' = NEt_2
h, X = Cl, Y = H, R' = Et, R'' = NMe_2
i, X = Cl, Y = H, R' = Et, R'' = $N(CH_2)_5$
j, X = Cl, Y = H, R' = Me, R'' = NMe_2
k, X = Cl, Y = H, R' = Me, R'' = NEt_2
l, X = Cl, Y = H, R' = Me, R'' = $N(CH_2)_5$
m, X = Y = Cl, R' = Me, R'' = NMe_2
n, X = Y = Cl, R' = Me, R'' = NEt_2
o, X = Y = Cl, R' = Me, R'' = $N(CH_2)_5$
p, X = Y = Cl, R' = Et, R'' = NEt_2
q, X = Y = Cl, R' = Et, R'' = NMe_2
r, X = Y = Cl, R' = Et, R'' = $N(CH_2)_5$



II



a, X = Y, R' = Me, R'' = NEt_2
b, X = Y, R' = Me, R'' = NMe_2
c, X = Y, R' = Me, R'' = $N(CH_2)_5$
d, X = Y, R' = Et, R'' = NEt_2
e, X = Y, R' = Et, R'' = NMe_2
f, X = Y, R' = Et, R'' = $N(CH_2)_5$
g, X = H, R' = Me, R'' = NMe_2
h, X = H, R' = Me, R'' = NEt_2
i, X = H, R' = Me, R'' = $N(CH_2)_5$
j, X = H, R' = Et, R'' = NEt_2
k, X = H, R' = Et, R'' = NMe_2
l, X = H, R' = Et, R'' = $N(CH_2)_5$
m, X = *p*-Chloroanilino, R' = Me, R'' = NMe_2
n, X = *p*-Chloroanilino, R' = Me, R'' = NEt_2
o, X = *p*-Chloroanilino, R' = Me, R'' = $N(CH_2)_5$
p, X = *p*-Chloroanilino, R' = Et, R'' = NEt_2
q, X = *p*-Chloroanilino, R' = Et, R'' = NMe_2
r, X = *p*-Chloroanilino, R' = Et, R'' = $N(CH_2)_5$

Table 1

Compd. no.	Dose in term of Q	Result against *P. gallinaceum*
IIm	4Q	active
	Q	inactive
	1/4Q	inactive
IIq	4Q	active
	Q	inactive
	1/4Q	inactive

of their antimalarial activity. The procedure adopted and the report (Table 2) of these compounds are given below.

Table 2

Compd. no.	Average % parasitemia
Ic	All animals died
Ig	10.2%
IVc	10.6%
Saline	20.6%
Chloroquine	8.8%

All the mice were inoculated with 10 million *Plasmodium berghei* parasitized mouse RBC. The blood smears of these animals were tested for the appearance of parasite. These animals were divided into 6 groups consisting of 6 animals each. All these animals were given different drugs at a dose 10 mg/kg body weight, for four days through subcutaneous route, starting on the day on which parasite appeared in the blood smear for the first time. Controls were treated with the normal saline only. On the day following the last dose of the drug, blood smears were made from each animal and stained with Leishman stain. The smears were examined for the parasitemia. The average percent parasitmia was calculated for each group. All the animals in the group treated with drug Ic died on the day following first dose of the drug.

Four compounds were tested for their antimalarial activity in the Post Graduate Institute of Medical Education and Research, Chandigarh. The following is the procedure adopted. Swiss albino male mice, 5-6 weeks old were inoculated intraperitonially with 1×10^6 *Plasmodium berghei* infected red blood cells. Tail smears of the animals stained with Giemsa were tested for the appearance of the parasite. These animals were divided into seven groups consisting of 4-5 animals each. All these animals were given different drugs in the concentration 0.3 mg/0.1 ml per dose for three days intraperitonially starting from the day when the animals showed a parasitemia of 3-5 percent. The control animals were treated with normal saline only. Chloroquine was taken as the control drug.

Compounds **Ig**, **Ii**, **IIb** and **IIr** were tested for antimalarial activity against *P. berghei* in mice, out of which **Ig** has shown promising results in arresting the growth of the parasite (Table 3).

Table 3

Compd. no.	Mean percentage parasitaemia		Percentage mortality			
	Before drug inoculation (day 3rd P.I.)	2 days after drug inoculation (day 7th P.I.)	5 days after drug inoculation (day 12th P.I.)	6th P.I.	10th P.I.	12th P.I.
Ig	4.1	0	25	—	25	75
Ii	5.0	4.0	35	33	—	67
IIb	5.0	6	all died	—	—	100
IIr	3.0	0	all died	—	50	50
Chloroquine	2.6	0	0	—	—	—
Control (without drug)	3.5	13.3	all died	25	50	25

P.I. = Post infection.

Further work on the evaluation of the various compounds is still in progress.

Experimental

2-Methyl-3-(3'-N-piperidinomethyl-4'-ethoxy) phenyl-4(3H)quinazoline **Ic** : A mixture of 1.6 g (0.01 mol) 2-methyl-3 : 1 : 4-benzoxazone and 2.44 g (0.01 mol) of 3-*N*-piperidino-methyl-4-ethoxy aniline was heated on water bath for 2 h. The mass obtained was washed with ether and filtered. It was crystallised from absolute alcohol to get **Ic** as white powder (1.2 g), m.p. 122-123° (Found : N, 11.0. $C_{23}H_{27}O_2N_3$ requires N, 11.14%) ; ν_{max} 3140, 2926, 2840, 1630, 1440, 1360, 1235, 770, 730, 700 cm^{-1}.

The remaining mass obtained from the mother liquor was treated with 5 ml perchloric acid and heated on a water bath for 1 h. The separated solid was filtered and dried. On crystallisation from a mixture of absolute alcohol and dry ether yielded the perchlorate salt of **Ic** as white powder (1 g), m.p. 148° (Found : N, 8.5. $C_{23}H_{27}O_2N_3.HClO_4$ requires N, 8.9%).

6,8-Dichloro-2-methyl-3-(3'-N-diethylaminomethyl-4'-methoxy)phenyl-4(3H) quinazolinone **In** : A mixture of 2.07 g (0.01 mol) 6,8-dicholoro-2-methyl-3 : 1 : 4-benzoxazone and 2.11 g (0.01 mol) 3*N*-diethylaminomethyl-4-methoxy aniline was heated on a water bath for 2-3 h. The resulting mass was filtered and dried. It was crystallised from absolute alcohol as brown powder (1.9 g), m.p. 105° (Found : C, 61.01 ; H, 5.5 ; N, 10.2. $C_{21}H_{23}N_3O_2Cl_2$ requires C, 60.0 ; H, 5.47 ; N, 10.01%).

The other 2-methyl-3-(substituted)-4 (3*H*) quinazolinones and 6-chloro-6,8-dichloro-2-methyl-3-(substituted)-4 (3*H*) quinazolinones were prepared in a similar manner. Their m.ps. yields, and analytical data are reported in Table 4.

4-Chloroquinazoline : 4-Quinazolone was obtained by heating anthranilic acid with excess of formamide[11]. This was then refluxed with phosphorus

TABLE 4

Compd. no.	Mold. formula	M.p. °C	Analysis % ; Found/(Calcd.) N	C	H	Cl	Solvent for crystallisation*
Ia	$C_{22}H_{17}O_2N_2$	115-116	11.80 (11.50)				A
Ib	$C_{20}H_{22}O_2N_2$	95-96	12.50 (12.46)				AE
Ic	$C_{22}H_{27}O_2N_2$	122-123	11.00 (11.14)				A
Id	$C_{21}H_{21}O_2N_2$	135-136	11.95 (11.96)				A
Ie	$C_{19}H_{21}O_2N_2$	104-105	12.08 (13.00)				A
If	$C_{22}H_{22}O_2N_2$	172	11.52 (11.57)				AE
Ig	$C_{22}H_{24}O_2N_2Cl$	115-116	10.66 (10.50)	66.01 (66.08)	6.45 (6.50)		A
Ih	$C_{20}H_{22}O_2N_2Cl$	127-128	11.42 (11.30)	64.75 (64.60)	5.91 (5.92)		A
Ii	$C_{22}H_{24}O_2N_2Cl$	138	10.18 (11.20)	67.10 (67.07)	6.09 (6.31)		A
Ij	$C_{19}H_{20}O_2N_2Cl$	124-125	11.50 (11.70)				A
Ik	$C_{21}H_{24}O_2N_2Cl$	108-109	11.89 (10.95)	65.20 (65.36)	6.15 (6.22)		A
Il	$C_{22}H_{24}O_2N_2Cl$	120	10 66 (10.56)	66.12 (66.41)	6.01 (6.08)		A
Im	$C_{19}H_{19}O_2N_2Cl_2$	115-116	10.72 (10.71)	58.25 (58.16)	4.56 (4.48)		A
In	$C_{21}H_{22}O_2N_2Cl_2$	105	10.20 (10.00)	61.00 (60.00)	5.50 (5.47)	19.50 (19.90)	A
Io	$C_{22}H_{22}O_2N_2Cl_2$	107	9.60 (9.70)	62.00 (61.11)	5.28 (5.32)		A
Ip	$C_{22}H_{26}O_2N_2Cl_2$	135	9.80 (9.67)				A
Iq	$C_{20}H_{21}O_2N_2Cl_2$	120	10.14 (10.30)				A
Ir	$C_{22}H_{22}O_2N_2Cl_2$	245	9.52 (9.40)				A
IIh	$C_{20}H_{24}ON_4.HCl$	256	15.01 (15.03)	64.70 (64.42)	4.40 (6.44)		B
IIg	$C_{19}H_{20}ON_4.HCl$	251-252	16.00 (16.25)				B
IIi	$C_{21}H_{24}ON_4.HCl$	261-262	14.62 (14.56)	65.55 (65.53)	6.03 (6.24)		B
IIj	$C_{21}H_{26}ON_4.HCl$	270-271	14.42 (14.48)				B
IIk	$C_{19}H_{22}ON_4.HCl$	219-220	15.55 (15.62)				B
IIl	$C_{22}H_{26}ON_4.HCl$	236-237	14.12 (14.05)	66.15 (66.24)	6.51 (6.52)		B
IIm	$C_{24}H_{24}ON_6Cl.2HCl$	252	13.50 (13.70)				A
IIn	$C_{26}H_{26}ON_6Cl.2HCl$	238-239	13.10 (13.00)				A
IIo	$C_{27}H_{28}ON_6Cl.2HCl$	265-266	12.60 (12.80)				A
IIp	$C_{27}H_{30}ON_6Cl.2HCl$	245-246	12.50 (12.70)				A
IIq	$C_{26}H_{28}ON_6Cl.2HCl$	272	13.30 (13.40)				A
IIr	$C_{28}H_{30}ON_6Cl.2HCl$	264	12.20 (12.60)				A
IIa	$C_{32}H_{42}O_2N_8.2HCl$	286	13.68 (13.65)				A
IIb	$C_{32}H_{44}O_2N_8.2HCl$	280	15.00 (15.02)			12.64 (12.60)	A
IIc	$C_{34}H_{42}O_2N_8.2HCl$	286	13.10 (13.14)			11.10 (11.11)	A
IId	$C_{34}H_{42}O_2N_8.2HCl$	262	13.00 (13.06)			11.00 (11.04)	C
IIe	$C_{30}H_{38}O_2N_8.2HCl$	250	14.20 (14.31)			12.01 (12.09)	A
IIf	$C_{36}H_{46}O_2N_8.2HCl$	256	12.61 (12.59)			10.60 (10.64)	A

* A = Absolute ethanol, B = Benzene, C = Ethanol, AE = Absolute ethanol-ether.

oxychloride and phosphorus pentachloride for 5.5 h. Phosphorus oxychloride was distilled off under reduced pressure. The residue was treated with ammonia and extracted with ether. Ether was evaporated when 4-chloroquinazoline was obtained.

4-(3′-4-Piperidinomethyl-4-ethoxy)anilino quinazoline hydrochloride **III** : It was prepared by refluxing 2.88 g (0.02 mol) 4-chloroquinazoline and 4.96 g (0.02 mol) 3*N*-piperidino-methyl-4-ethoxy aniline for 3 h in the presence of 20 ml benzene. Benzene was then distilled off and the residue was filtered and dried. It was crystallised from benzene into a white powder (1.4 g), m.p. 236-237° (Found : C, 66.15 ; H, 6.51 ; N, 14.12. $C_{22}H_{26}ON_4$.HCl requires C, 66.24 ; H, 6.52 ; N, 14.05%).

The other 4-substituted quinazolines were prepared similarly.

2-p-*Chloroanilino-4-chloro-quinazoline* : 2 : 4- Dihydroxy quinazoline[12] was refluxed with phosphorus oxychloride and phosphorus pentachloride to get 2 : 4-dichloroquinazoline which was then stirred with 2*N* sodium hydroxide solution to form 2-chloro-4-hydroxy quinazoline. This was then refluxed with chloroaniline, water, acetone and hydrochloric acid to form 2-*p*-chloroanilino-4-hydroxy quinazoline. 2-*p*-Chloroanilino-4-hydroxy quinazoline was refluxed with phosphorus oxychloride and phosphorus pentachloride to form 2-*p*-chloroanilino-4-chloroquinazoline.

2-p-*Chloroanilino-4-(3′-*N*-dimethylamine-methyl-4′-ethoxy) anilino quinazoline dihydrochloride* **IIg** : It was prepared by heating 1.2 g (0.004 mol) 4-chloro-2-*p*-chloroanilinoquinazoline with 0.776 g. (0.004 mol) 3-*N*-dimethylamino-methyl-4-ethoxy aniline in the presence of 5 ml glacial acetic acid on a water bath for 2 h. The solution was then diluted with 20 ml water, boiled and filtered and then 5 ml conc. hydrochloric acid was added to it. It was then allowed to stand for 2 h in an ice bath. The dihydrochloride separated out was dissolved in alcohol by boiling, charcoalised and filtered. Upon standing the desired compound separated as a white powder (0.75 g), m.p. 272° (Found : N, 13.3. $C_{25}H_{26}N_5$OCl.2HCl requires N, 13.4%).

The other 2-*p*-chloroanilino-4-substituted quinazolines were prepared similarly.

*2 : 4-Di(3′-*N*-piperidino methyl-4′-ethoxyanilino) quinazoline dihydrochloride* **IIf** : It was prepared by heating 0.796 g (0.004 mol) 2 : 4-dichloroquinazoline and 0.936 g (0.004 mol) 3*N*-piperidinomethyl-4′-ethoxy aniline in the presence of dry benzene on a water bath for 2 h. The mass was chilled in ice when the desired product separated out. It was filtered, dried and crystallised from absolute alcohol into yellow powder (0.45 g), m.p. 256° (Found : N, 12.61 ; Cl, 10.60. $C_{36}H_{46}N_6O_2$.2HCl requires N, 12.59 ; Cl, 10.64%).

The other 2 : 4-disubstituted quinazolines were prepared similarly.

Acknowledgement

One of the authors (N.S.) is thankful to the C.S.I.R., New Delhi for the award of Junior Research Fellowship and the authors are also thankful to the Chairman of the Department of Chemical Engineering and Technology, Panjab University, for providing the necessary facilities.

References

1. O. PRICE and M. ROYSTON, *J. Am. Chem. Soc.*, 1946, **68**, 1904.
2. E. A. STECK, L. L. HALLOCK and O. M. SUTER, *J. Am. Chem. Soc.*, 1938, **70**, 4063.
3. A. R. SURREY and H. F. HAMMER, *J. Am. Chem. Soc.*, 1950, **72**, 1814.
4. P. N. NATARANJAN and LEN NGIAM TONG, *J. Med. Chem.*, 1972, **15**, 829.
5. J. H. BURCKHALTER, F. H. TENDICK, E. M. JONES, P. A. JONES, W. F. HOLCOMB and A. L. RAWLINS, *J. Am. Chem. Soc.*, 1948, **70**, 1363.
6. J. B. KOEPFLI, J. A. BROCKMAN, JR. and J. MOFFAT, *J. Am. Chem. Soc.*, 1950, **72**, 3323.
7. P. SINGH and I. S. GUPTA, *J. Indian Chem. Soc.*, 1979, **56**, 77.
8. D. T. ZENTMEYER and E. C. WAGNER, *J. Org. Chem.*, 1949, **14**, 967.
9. J. H. BURCKHALTER, F. H. TENDICK, E. M. JONES, P. A. JONES, W. F. HOLCOMB and A. L. RAWLINS, *J. Am. Chem. Soc.*, 1948, **70**, 1371.
10. L. M. SHERRILL, E. ELISBERG and E. M. SMITH, *J. Am. Chem. Soc.*, 1946, **68**, 1301.
11. L. M. SHERRILL, E. ELISBERG and E. M. SMITH, *J. Am. Chem. Soc.*, 1946, **68**, 1800.
12. F. H. S. CURD, J. A. LANDQUIST and F. L. ROSE, *J. Am. Chem. Soc.*, 1947, **69**, 777.

NOTES

Palladium(II) Pyridine Complexes Containing Trifluoro and Hexafluoroacetylacetonate as Counter Ions

B. K. SAHU, G. C. DASH and B. K. MOHAPATRA*

Department of Chemistry, B. J. B. College, Bhubaneswar-751 014

Manuscript received 11 May 1981, revised 9 December 1983, accepted 17 June 1984

BIS(acetylacetonato)palladium(II)[1] and bis(ethyl-acetoacetato)palladium(II)[2] react with equimolar amount of a number of bases to transform one of the chelating ligands into the central carbon(C^3) bonded state. Whereas reaction of bis(acetylacetonato)palladium(II) with excess amines results in expelling the β-diketonate ligand from the coordination sphere either partly or fully giving rise to complexes having β-diketonate anions[3]. We have been studying the various linkage modes[4-7] of β-diketones in palladium(II) and platinum(II) complexes. As a part of this programme, reaction of bis(hexafluoroacetylacetonato)palladium(II) and bis(trifluoroacetylacetonato)palladium(II) with a number of nitrogen and phosphorus bases was studied. This communication reports the reaction of $Pd(hfac)_2$ and $Pd(tfac)_2$ with substituted pyridines resulting in complexes of the composition $[PdL_4]X_2$, where L is the heterocyclic base and X is the β-diketonate anion.

Experimental

Hexa- or trifluoroacetylacetone was dissolved in equimolar amount of methanolic KOH and the solution slowly evaporated to dryness and then extracted with water. A solution of K_2PdCl_4 was reacted with the above ligands in 1 : 2 proportion and stirred for 1 h. The precipitate of $Pd(hfac)_2$ was filtered off, dried in vacuum and extracted with ether. Etherial extract was filtered out and the product crystallised by slow atmospheric evaporation. In case of $Pd(tfac)_2$, the dried precipitate was extracted with dichloromethane, filtered and the product was crystallised from the filtrate.

$Pd(hfac)_2$ (0.3 g) was stirred with γ-picoline 3 cc at 40° till it dissolved. The solution was kept in freeze overnight when light yellow crystals were obtained and recrystallised from dichloromethane-petroleum ether. The yield was almost quantitative (~90%). $Pd(hfac)_2$ and $Pd(tfac)_2$ were reacted with various bases in the similar manner and the products were obtained in 80-90% yield depending on the bases.

Analytical and physical measurements were done (Table 1) as reported earlier[4].

TABLE 1—ANALYTICAL DATA OF COMPLEXES

Sl. no.	Compounds	M.p. °C	Analysis %; Found/(Calcd.) C	H	N	Λ_M $\Omega^{-1}cm^2$
1.	$[Pd(\gamma\text{-pic})_4](hfac)_2$	165	45.64	3.21	6.15	180
2.	$[Pd(\beta\text{-pic})_4](hfac)_2$	163	45.58 (45.72)	3.18 (3.36)	6.12 (6.28)	192
3.	$[Pd(\alpha\text{-pic})_4](hfac)_2$	174	45.62	3.15	6.11	185
4.	$[Pd(\gamma\text{-pic})_4](tfac)_2$	175	51.88	4.41	6.88	198
5.	$[Pd(\beta\text{-pic})_4](tfac)_2$	170	51.85 (52.01)	4.45 (4.59)	6.85 (7.14)	200
6.	$[Pd(\alpha\text{-pic})_4](tfac)_2$	178	51.90	4.88	6.92	186
7.	$[Pd(2,6\text{-lut})_4](hfac)_2$	156	47.95 (48.08)	3.82 (4.01)	5.71 (5.90)	188
8.	$[Pd(2,6\text{-lut})_4](tfac)_2$	158	54.11 (54.26)	5.08 (5.24)	6.48 (6.66)	197

hfac = Anion of hexafluoroacetylacetone, tfac = Anion of trifluoroacetylacetone.

Results and Discussion

On the basis of analysis, the complexes reveal the composition $[PdL_4]X_2$, where L is the nitrogen base and X is the β-diketonate anion. These are all yellow or light yellow crystalline solids soluble in acetone, chloroform and dichloromethane. In the infrared spectra of $Pd(hfac)_2$, three bands are observed at 1590, 1545, 1520 cm^{-1} and in the case of $Pd(tfac)_2$ two bands at 1600 and 1530 cm^{-1}, due to C=O and C=C stretching modes. In case of $[PdL_4](hfac)_2$ type of complexes these bands are noticed at ~1680, 1630 and 1540 cm^{-1}, and in $[PdL_4](tfac)_2$ type of complexes at 1630, 1550 and 1510 cm^{-1}. Bands in the carbonyl stretching region almost coincide with those of the corresponding potassium β-diketonates. This indicates that the β-diketonates are not chelated, but are present as anions in the outer sphere. This has been further supported by the molar conductance data in acetone (Table 1) indicating 1 : 2 electrolytic nature. There are many absorption bands due to coordinated substituted pyridines. But the most characteristic band due to pyridine ring vibration appears in ~1610-1618 cm^{-1} region. In the far infrared region ν_{Pd-N} is observed at ~330 cm^{-1} region[8] confirming the coordination of only the nitrogen atoms of the bases.

In the ^1H nmr spectra, methine proton signals of hfac anion appear above 5.9 ppm. Methine and methyl proton signals of tfac anion appear at ~5.6-5.8 and 2.2 ppm, respectively. Usually, methine proton of β-diketonate anion resonates in

higher field (low ppm scale) than chelated β-diketone. Hence, in conformity with earlier observations[8], this confirms the presence of β-diketonate anions in the outer sphere. In addition to the above signal CH_3 and CH group proton signals of coordinated substituted pyridine, are observed at ~2.4 and 8-9 ppm, respectively.

In solution, $[PdL_4](ac.ac)_2$ type complexes usually dissociate to give $[PdL_2(ac.ac)](ac.ac)$ or $Pd(ac.ac)(C^3\text{-}ac.ac)L$ type complexes. But $[PdL_4](hfac)_2$ and $[PdL_4](tfac)_2$ type complexes are stable in solution. Thus, in solution state, the relative stability of compounds containing β-diketonate anion in the outer sphere is in the order: ac.ac < tfac < hfac[9], which is in accordance with the relative acid strength of the β-diketones[10].

Acknowledgement

Thanks are due to U.G.C., New Delhi, for financial assistance.

References

1. S. Baba, T. Ogura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 665.
2. M. Horike, Y. Kai, N. Yasuoka and N. Kasai, *J. Organomet. Chem.*, 1974, **72**, 441; S. Okeya and S. Kawaguchi, *Inorg. Chem.*, 1977, **16**, 1780.
3. S. Okeya, Y. Onuki, Y. Nakamura and S. Kawaguchi, *Chem. Lett. Jpn.*, 1977, 1305.
4. B. K. Sahu and B K. Mohapatra, *Z. Anorg. Allg. Chem.*, in press.
5. B. K. Sahu and B. K. Mohapatra, *J. Less-Common Met.*, in press.
6. B. K. Mohapatra, *Aust. J. Chem.*, communicated.
7. B. K. Sahu and B. K. Mohapatra, *Acta Chim. (Budapest)*, communicated.
8. J. R. Ferraro, "Low Frequency Vibration of Inorganic and Coordination Compounds", Plenum Press, New York, 1971.
9. S. Komiya and J. K. Kochi, *J. Am. Chem. Soc.*, 1977, **99**, 8695.
10. J B. Jones and S. P. Patel, *J. Am. Chem. Soc.*, 1974, **96**, 574.

Palladium(II) and Cobalt(III) Complexes of *p*-chloroisonitrosobenzoylacetone and *p*-bromoisonitrosobenzoylacetone

B. J. Desai and V. M. Shinde*

Department of Chemistry, Shivaji University, Kolhapur-416 004

Manuscript received 30 May 1981, revised 6 April 1983, accepted 17 June 1984

p-CHLOROISONITROSOBENZOYLACETONE (*p*-Cl INBA) and *p*-bromoisonitrosobenzoylacetone (*p*-Br INBA) have been used as chromogenic reagents for palladium and ruthenium[1]. However, structural investigations on the complexes of these ligands are lacking. In this communication we report the synthesis of solid complexes of palladium(II) and cobalt(III) with *p*-Cl INBA and *p*-Br INBA and their characterization on the basis of magnetic susceptibility measurements, ir, uv and pmr data.

* Department of Chemistry, Institute of Science, Bombay.

Experimental

Physical measurements : Magnetic susceptibility of the complexes was measured by Gouy method using mercury tetrathiocyanatocobaltate(II) as the calibrant. Ir spectra (nujol) were recorded on Perkin-Elmer Model 221 spectrophotometer. The electronic spectra were taken on a Beckman DU-2 recording spectrophotometer and pmr spectra ($CDCl_3$) were recorded using Varian spectrometer (100 MHZ) with TMS as internal standard.

The molecular weights of the complexes were determined by cryoscopic method.

Synthesis of ligands : *p*-Cl INBA(I) and *p*-Br INBA(II) were synthesised by dropwise addition of sodium nitrite solution (4.6 g in minimum amount of water) to a solution of *p*-chloro- or *p*-bromobenzoylacetone (~10 g) dissolved in 30 ml of acetic acid. The reaction mixture was constantly stirred at < 5° and then poured into ice water when white crystals precipitate out. The crystals were collected, washed with water and recrystallised from methanol.

Synthesis of palladium and cobalt complexes of p-*Cl INBA and* p-*Br INBA :* The palladium and cobalt complexes were prepared by reacting aqueous solution of metal chlorides with ethanolic solution of *p*-Cl INBA and *p*-Br INBA in 1 : 2 and 1 : 3 molar ratios, respectively, followed by dropwise addition of either sodium acetate (for Pd, *p*H 4) or sodium hydroxide (for Co, *p*H 6) solutions till the orange-red or yellow-orange complexes precipitate out. The precipitated compounds were filtered under suction, washed with ethanol and dried in vacuum.

Results and Discussion

The palladium and cobalt complexes were found to be soluble in chloroform, benzene, ethylacetate, methanol and acetone, and insoluble in water, carbontetrachloride and petroleum ether. The analytical results (Table 1) and the molecular weights of the palladium and cobalt complexes correspond to the composition of PdL_2 and CoL_3, respectively. Similarly, the magnetic measurements have shown them to be dimagnetic. Therefore, palladium complexes must have planer structure whereas cobalt complexes should be octahedral. Cobalt(II) thus gets oxidized to cobalt(III) during complexation with isonitroso compounds.

Pmr spectra of palladium(II) and cobalt(III) complexes in $CDCl_3$ exhibit phenyl proton resonance signals in the range 2.2 to 2.6 τ and methyl signals in the range 7.35 to 7.5 τ. The proton signal due to NOH observed in the ligands (Table 1) at 1.84-1.86 τ, however, disappear in the complexes suggesting that the complexation leads to the replacement of the oxime proton by the metal ion.

The selected ir bands of the ligands and the complexes are given in Table 2. The OH stretching

TABLE 1—ANALYTICAL DATA, PMR SIGNALS AND ELECTRONIC ABSORPTION BANDS OF LIGANDS AND THEIR COMPLEXES

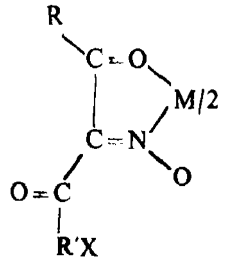
Compd.	Decom. temp. °C	Analysis % : Found/(Calcd.) N	Halogen	M	Pmr signals τ	λ_{max} (MeOH) kK(ε)
p-Cl INBA	160*	6.25 (6.20)	15.7 (15.5)	— —	1.84, 2.2-2.6, 7.5	39.5 (12790)
p-Br INBA	164*	5.18 (5.10)	29.6 (29.5)	— —	1.86, 2.2-2.45, 7.85	38.0 (16900)
Bis(p-Cl INBA)Pd^{II}	196	5.0 (5.0)	12.6 (12.7)	19.0 (19.1)	— 2.4-2.7, 7.5	39.0 (26440) 25.0 (5288)
Bis(p-Br INBA)Pd^{II}	196	4.4 (4.8)	24.7 (24.7)	16.4 (16.5)	— 2.2-2 45, 7.85	38.0 (20300) 25.0 (8706)
Tris(p-Cl INBA)Co^{III}	200	5.8 (5.7)	14.4 (14.5)	7.9 (8.0)	— 2.1-2.6, 7.85	40.8 (28960) 35.8 (28210) 27.7 (12460)
Tris(p-Br INBA)Co^{III}	200	5.0 (4.8)	27.5 (27.7)	6.7 (6.8)	— 2.2-2.45, 7.85	39.8 (27940) 36.8 (19440) 27.7 (9959)

* Melting point.

TABLE 2—SOME IMPORTANT VIBRATIONAL BANDS AND ASSIGNMENTS IN LIGANDS AND THEIR COMPLEXES

p-Cl INBA	Pd^{II} (p-Cl INBA)$_2$	Co^{III} (p-Cl INBA)$_3$	p-Br INBA	Pd^{II} (p-Br INBA)$_2$	Co^{III} (p-Br INBA)$_3$	Assignment
3380,s	—	—	3275 s	—	—	Hydrogen bonded OH stretching of C=NOH
1675 s	1650 s	1650 s	1670 s	1645 m	1650 s	C=O stretching
1620 m	—	—	1610 m	—	—	C=N stretching
1590 s	1590 m	1590 m	1580 s	1580 w	1590 m	Perturbed C=N stretching
—	1525 m	1525 m	—	1510 w	1520 m	Bonded C=O stretching
1225 w	1225 s	1225 s	1225 w	1230 m	1230 m	NO stretching
1090 s	1080 m	1085 s	1070 s	1065 s	1065 m	ON stretching

frequency exhibited by the ligands disappears in the palladium and cobalt complexes and confirms the result of pmr studies that the complex formation involves replacement of the hydrogen atom of the NOH group by the metal atom. The strong band at 1650-1645 cm^{-1} in metal complexes is assigned to C=O of the aromatic ketone and is indicative of the symmetric nature of the complexes. The weak band at 1620-1610 cm^{-1} in the ligand is assigned to C=N stretching[2], which shifts to 1590-1580 cm^{-1} in the metal complexes. The band at 1525-1510 cm^{-1} in the complexes is assigned to bonded C=O stretching. The band at 1230-1225 cm^{-1} may be tentatively attributed to N-oxide stretching frequency. This is consistent with the fact that the N-oxide peak in aromatic ring compounds occurs as a strong band in the region 1300-1200 cm^{-1}. Further it is reported that tris(dimethylglyoximinato)-cobalt(III)[3] and tris(isonitrosoacetylacetonato)-cobalt(III)[4] having 5-membered ring structures, exhibit N-oxide band at 1221 and 1292 cm^{-1}, respectively. The ir and pmr data suggest that the dimagnetic palladium and cobalt complexes of p-Cl INBA and p-Br INBA may be formulated by the following structures.



where, R is CH_3, R' is C_6H_5 group containing either Cl or Br, and M may be Pd^{II} or Co^{III}.

The electronic spectra of the ligands in chloroform exhibit an intense band at 39.5 kK (p-Cl INBA) and 38.0 kK (p-Br INBA). This band is attributed to $\pi \rightarrow \pi^*$ transition in the ligand. The palladium complexes show one additional band at 25 kK which can be assigned to charge transfer transition. The charge transfer transition in cobalt(III) complexes, however, occurs at 27.7 kK. In view of the high intensity of charge transfer transitions the d-d bands are obscured and are not visible in the absorption spectrum of the complexes.

References

1. V. V. Yeole, A. D. Langade and V. M. Shinde, *Mikrochim. Acta*, in press.
2. K. Nakanishi, "Infrared Absorption Spectroscopy", Nankodo, Tokyo, 1964, p. 51.
3. K. Burger, L. Buff and F. Ruff, *J. Inorg. Nucl. Chem.*, 1965, **27**, 179.
4. N. J. Patil and B. C. Haldar, *J. Inorg. Nucl. Chem.*, 1967, **20**, 1037.

Cobalt(II) and Zinc(II) Phenylacetate Complexes with Nitrogen Donor Ligands

BISWESWAR DAS* and P. C. ROY

Department of Chemistry, Government College, Rourkela-769 004

Manuscript received 27 June 1983, revised 20 February 1984, accepted 21 July 1984

THORNTON *et al.* have reported[1] some Ni^{II} complexes of benzoates and substituted benzoates with heterocyclic amine ligands. More recently Guru *et el.* have also reported[2] some phenylacetate complexes of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} with nitrogen donor ligands. In the present communication we report some mixed ligand complexes of Co^{II} and Zn^{II} phenylacetates with different nitrogen donor ligands.

Experimental

Ethanolic solutions of Zn^{II} and Co^{II} phenylacetates were mixed with different nitrogen donor ligands in stoichiometric ratio and the resulting solutions were refluxed on water bath for 2 h. The 2,2'-dipyridine and 1,10-phenanthroline complexes separated out on shaking and cooling, while the pyridine and γ-picoline complexes were obtained after keeping the solution for more than 24 h. The complexes were filtered under suction, washed with ethanol and ether and dried over anhydrous $CaCl_2$ in a vacuum desiccator.

Results and Discussion

All the complexes of zinc are white crystalline solid and those of cobalt are pink crystalline and have the composition ML_2B_2 or ML_2B', where B = pyridine and γ-picoline and B' = 2,2'-dipyridyl and 1,10-phenanthroline. The compounds are soluble in acetone in which medium they behave as non-electrolyte, as the Λ_M values are low being 9 to 15 Ω^{-1} cm^2 (Table 1). All the cobalt(II) compounds are paramagnetic with μ_{eff} values 4.9 to 5.1 B.M. indicating the octahedral stereochemistry. The high spin octahedral cobalt(II) complexes have[3] large orbital contributions to spin only values and the magnetic moments are found to vary from 4.7 to 5.2 B.M. The high orbital contribution is attributable to the three-fold orbital degenerecy of the $^4T_{1g}$ ground state.

In free sodium phenylacetate asymmetric and symmetric C=O stretching frequencies appear at 1610 and 1400 cm^{-1}, respectively[4]. In metal phenylacetates these bands appear slightly to a lower frequency region, but again shifts to higher frequency region in case of mixed ligand complexes indicating that both phenylacetate and the nitrogen donor ligands are bonded to the metal ion. Further, most of the absorption bands due to free nitrogen ligands are also modified indicating[5] their coordination to the metal ion. The far ir spectra of the three complexes exhibit two bands at ~350 ν(M – N) and ~250 cm^{-1} ν(M – O). These bands further confirm that both phenylacetate and nitrogen donor ligands are bonded to the metal ion. The difference between the asymmetric and symmetric stretching $\nu_{C=O}$ mode of complexes are of the order 210-220 cm^{-1} indicating the bidentate nature of the phenylacetate as this difference will be of higher order for monodentate acetate group.

TABLE 1—ANALYSIS, CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA OF COMPLEXES

Compd.	Colour and form	Λ_0 Ω^{-1} cm^2	μ_{eff} B.M.	Analysis % ; Found/(Calcd.) M	N
$CoL_2(Py)_2$	Pink crystalline	9.5	4.80	12.00 (12.04)	5.68 (5.72)
$CoL_2(\gamma\text{-Pic})_2$	Pink crystalline	10.0	5.10	11.32 (11.40)	5.40 (5.44)
CoL_2(2,2'-Dipy)	Pink crystalline	11.2	4.96	11.97 (12.04)	5.65 (5.72)
CoL_2(1,10-Phen)	Rosy crystalline	11.8	4.96	11.92 (11.56)	5.47 (5.49)
$ZnL_2(Py)_2$	White crystalline	13.0	—	13.10 (13.18)	5.60 (5.65)
$ZnL_2(\gamma\text{-Pic})_2$	White crystalline	14.5	—	12.45 (12.54)	5.30 (5.37)
ZnL_2(2,2'-Dipy)	White crystalline	14.0	—	13.05 (13.18)	5.60 (5.65)
ZnL_2(1,10-Phen)	White crystalline	13.8	—	12.60 (12.67)	5.38 (5.42)

* Regional Research Laboratory, Bhubaneswar-751 013.

Cobalt(II) complexes give rise to two bands around 18,000 and 20,000 cm^{-1} which can be assigned to ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition characteristic of octahedral Co^{II} ion in O_h symmetry[5,6]. Electronic spectra and μ_{eff} values are in conformity with the high spin octahedral configuration of cobalt(II) complexes.

Infrared spectral data indicate that zinc complexes have an octahedral environment around the metal ion involving bidentate acetate group and the nitrogen donor ligands.

References

1. J. CATTERICK and P. THORNTON, *J. Chem. Soc., Dalton Trans.*, 1976, 233.
2. C. D. RAO, B. K. MOHAPATRA and S. GURU, *J. Indian Chem. Soc.*, 1979, **56**, 631.
3. F. A. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry", Willey Eastern, New Delhi, 1969, p. 870.
4. R. M. SILVERSTEIN and G. C. BASSLER, "Spectrophotometric Identification of Organic Compounds", John Willey, New York, 1967.
5. J. R. FERRARO, "Low Frequency Vibration of Inorganic and Coordination Compounds", Plenum Press, New York, 1977.
6. A. B. P. LEVER, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.

Complexing Behaviour of Some New Schiff Bases : High Spin Cobalt(II) and Nickel(II) Complexes with Tridentate and Tetradentate Schiff Base Ligands

UMA AGARWAL and GREESH SAXENA*

Chemical Research Laboratories, R B S. College, Agra-282 002

Manuscript received 16 June 1983, revised 9 March 1984, accepted 30 May 1984

THE synthesis, structural investigations and reactions of metal chelates with sulphur containing Schiff's bases have received renewed attention in recent years because of their proven antitumour[1,2] and carcinostatic activities[3,4]. Coordination compounds of cobalt(II) and nickel(II) with various Schiff bases have been studied extensively[5-8] but little is known about the complexes of Schiff bases derived from heterocyclic glyoxalic aldehydes. Hence, an attempt has been made here to prepare and characterise nickel(II) and cobalt(II) chelates with Schiff bases derived from 2-acetyl thiophene glyoxal and various amines.

Experimental

All the chemicals were of AnalaR grade. 2-Acetyl thiophene glyoxal was prepared by the reported method[9]. The ligands were prepared by the condensation of 2-acetyl thiophene glyoxal with *p*-aminobenzoic acid, *p*-toluidine, 2-aminopyridine and *o*-phenylenediamine in absolute ethanol. These were purified by recrystallisation from absolute ethanol. Complexes were prepared by mixing ethanolic solutions of ligands and metal chlorides in 1 : 1 and 2 : 1 molar ratio. The mixture was refluxed on a water bath for 1-4 h and then concentrated to a small volume. On cooling, crystals of the complexes obtained were filtered, washed with water and ethanol and dried in air.

The analyses of carbon and hydrogen were done at C.D.R.I., Lucknow. Nitrogen was estimated by Kjeldahl's method. Metals were estimated by Vogel's method[10] after decomposing the complex with a mixture of H_2SO_4 and HNO_3. Magnetic susceptibility measurements were made by Gouy method at room temperature (288 K) using water as calibrant. Dimagnetic corrections were made by using Pascal's constants. Electronic spectra were recorded in acetone on Toshniwal visible spectrophotometer. Ir spectra were recorded in nujol on a Perkin-Elmer model 621 spectrophotometer.

Results and Discussion

The complexes under investigation are listed in Table 1 along with their colour, analysis and other properties. Analytical data of these complexes reveal 1 : 1 and 1 : 2 (metal : ligand) stoichiometry. The molar conductance values (3.78-12.6 Ω^{-1} cm^2 mol^{-1}) in acetone solution adequately confirm the non-ionic nature of the complexes[11]. The magnetic moments of cobalt(II) and nickel(II) complexes are in the ranges 4.65-5.05 and 2.98-3.25 B.M., respectively indicating the spin-free octahedral geometry around the metal ions[12].

The cobalt(II) complexes show two d-d bands in 15151-16260 and 18181-19610 cm^{-1} regions which may be attributed to transitions ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3), respectively. ν_1 was not observed due to instrumental limitation. ν_1 was calculated by the method (C)[13] using the calculated values of 10 Dq and B (Table 2).

The values of transitions ν_1, ν_2 and ν_3 may be obtained by Konig's equations[14,15]. The ligand field parameter B and the ligand field splitting energy (10 Dq) in case of cobalt(II) complexes were calculated[16]. Out of the four methods applicable in case of Cobalt(II) complexes, the best fitting method is 13C because the ratio ν_2 (obs)/ν_1 (calcd.) is found to be around 2.14-2.15 as required for octahedral cobalt(II) complexes, and the calculated values of 10Dq is in good agreement to that determined by ν_2 (obs) $-$ ν_1 (calcd.). The values of β of these complexes are between 0.5-1.0 and clearly indicate the partial covalent character of the bond concerned. However, the electronic spectral data suggest octahedral geometry for all the complexes[17].

The electronic spectra of nickel(II) complexes (Table 3) are consistent with their octahedral geometry showing three d-d transition bands in 10526-11364, 16129-17241 and 25000-27777 cm^{-1} regions

TABLE 1—PHYSICAL CHARACTERISTICS AND ANALYTICAL DATA OF COBALT(II) AND NICKEL(II) SCHIFF BASE COMPLEXES

Sl. no.	Compd.	M.p. °C	Colour	Λ_M Ω^{-1} cm^{-2} mol^{-1}	Analysis % ; Found/(Calcd.) C	H	N	S	M	Cl	μ_{eff} B.M.
1.	$[Co(C_{13}H_9O_2NS)(H_2O)_2]$	218	Brownish black	4.65	44.60 (44.20)	3.82 (3.40)	3.84 (3.97)	9.18 (9.07)	16.58 (16.70)	—	4.82
2.	$[Co(C_{13}H_{11}ONS)_2]$	230	Dark brown	3.78	60.48 (60.86)	4.14 (4.26)	5.52 (5.42)	12.27 (12.38)	11.45 (11.39)	—	4.65
3.	$[Co(C_{11}H_9ON_2S)_2]$	226[d]	Green	7.22	53.69 (53.78)	3.32 (3.26)	11.52 (11.41)	13.11 (13.04)	12.12 (12.00)	—	4.98
4.	$[Co(C_{18}H_{12}O_2N_2S_2)Cl_2]$	228	Green	8.15	44.84 (44.82)	2.36 (2.49)	5.78 (5.81)	13.24 (13.28)	12.17 (12.23)	14.82 (14.73)	5.05
5.	$[Ni(C_{13}H_9O_2NS)(H_2O)_2]$	245[d]	Black	3.82	44.36 (44.20)	3.37 (3.40)	3.82 (3.97)	9.16 (9.07)	16.58 (16.64)	—	2.98
6.	$[Ni(C_{13}H_{11}ONS)_2]$	236	Black	2.56	60.32 (60.38)	4.16 (4.26)	5.54 (5.42)	12.29 (12.39)	11.44 (11.36)	—	3.25
7.	$[Ni(C_{11}H_9ON_2S)_2]$	198	Greenish yellow	3.64	53.78 (53.88)	3.35 (3.26)	11.39 (11.41)	13.14 (13.04)	11.88 (11.96)	—	3.16
8.	$[Ni(C_{18}H_{12}O_2N_2S_2)Cl_2]$	181	Yellowish	1.71	44.78 (44.84)	2.41 (2.49)	5.76 (5.81)	13.12 (13.29)	12.22 (12.19)	14.88 (14.74)	3.05

d = decomposed.

TABLE 2—OBSERVED AND CALCULATED TRANSITION ENERGIES (cm^{-1}) FOR THE COBALT(II) COMPLEXES

Methods of calculation	ν_1	ν_2	ν_3	B_{35}	10Dq	$\delta\nu$	β_{35}	$(\nu_2-\nu_1)$	ν_2/ν_1	$\delta\nu$%	CFSE kcal mol^{-1}
					$[Co(C_{13}H_9O_2NS)(H_2O)_2]$						
Experimental	—	15151	18181	—	—	—	—	—	—	—	—
(a)	fitted	fitted	18242	814	8088	+67	0.84	—	—	0.37	—
(h)	fitted	17350	fitted	887	9250	+2199	0.91	—	—	12.67	—
(c)	7063	fitted	fitted	809	8085	—	0.83	8088	2.15	—	18.48
(d)	7063	15151	18181	810	8088	—	0.83	—	—	—	—
					$[Co(C_{13}H_{11}ONS)_2]$						
Experimental	—	16129	19305	—	—	—	—	—	—	—	—
(a)	fitted	fitted	19319	859	8608	+14	0.88	—	—	0.07	—
(b)	fitted	18481	fitted	941	9852	+2852	0.97	—	—	12.78	—
(c)	7521	fitted	fitted	858	8606	—	0.88	8608	2.14	—	19.68
(d)	7521	16129	19305	858	8608	—	0.88	—	—	—	—
					$[Co(C_{11}H_9ON_2S)_2]$						
Experimental	—	15873	18691	—	—	—	—	—	—	—	—
(a)	fitted	fitted	18552	813	8468	−139	0.84	—	—	0.75	—
(b)	fitted	18244	fitted	906	9719	+2371	0.93	—	—	12.99	—
(c)	7410	fitted	fitted	823	8467	—	0.85	8463	2.14	—	19.35
(d)	7410	15873	18691	822	8463	—	0.85	—	—	—	—
					$[Co(C_{18}H_{12}O_2N_2S_2)Cl_2]$						
Experimental	—	16260	19610	—	—	—	—	—	—	—	—
(a)	fitted	fitted	19704	882	8682	+94	0.91	—	—	0.45	—
(b)	fitted	18624	fitted	959	9931	+2368	0.99	—	—	12.69	—
(c)	7578	fitted	fitted	875	8678	—	0.90	8682	2.15	—	19.88
(d)	7578	16260	19610	876	8682	—	0.90	—	—	—	—

assignable to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively[18].

The interelectronic repulsion parameter B in case of Ni^{II} complexes has been obtained by different methods[19]. Transition energies calculated according to different methods show that the best fit procedure is method (C)[18] as there is small difference in calculated transition energy and observed band energy. Electronic spectral data were used to calculate the important ligand field parameters 10Dq, β and λ. For d^8 complexes with O_h symmetry, Lever[20] suggested that the configuration interaction between $T_{1g}(P)$ and $T_{1g}(F)$ excited states lower the ratio ν_2/ν_1 from 1.8 (theoretical) to 1.5-1.7, which is in conformity with the experimental data supporting the distortion in octahedral geometry.

The infrared frequencies of the Schiff bases and their corresponding cobalt(II) and nickel(II) complexes are listed in Table 4. The frequencies in the free ligands at 1590-1630 (HC=N) and 1660-1720

TABLE 3—ELECTRONIC SPECTRAL DATA AND VARIOUS LIGAND FIELD PARAMETERS OF NICKEL(II) COMPLEXES

Methods of calculation	ν_1	ν_2	ν_3	B_{35}	β_{35}	$\delta\nu$	10Dq/B	λ	ν_2/ν_1	ν_3/ν_1	f	hx	CFSE kcal mol^{-1}	μ_{eff} Calcd. B.M.
							[$Ni(C_{18}H_9O_3NS)(H_2O)_2$]							
Experimental	10526	17241	26316	—	—	—	—	—	1.64	2.50	1.18	—	36.09	3.17
(a)	10Dq	fitted	29337	1000	0.96	+3021	10.53	164	—	—	—	0.33	—	—
(b)	10Dq	16541	fitted	752	0.72	−700	13.99	—	—	—	—	2.33	—	—
(c)	10Dq	16702	26846	798	0.77	+530	13.19	—	—	—	—	1.92	—	—
(d)	10Dq	16103	25180	647	0.62	−1136	16.27	—	—	—	—	3.17	—	—
							[$Ni(C_{18}H_{11}ONS)_2$]							
Experimental	10638	17241	27777	—	—	—	—	—	1.62	2.61	1.19	—	36.47	3.17
(a)	10Dq	fitted	28639	931	0.84	+862	11.43	195	—	—	—	0.92	—	—
(b)	10Dq	17050	fitted	861	0.83	−191	12.36	—	—	—	—	1.42	—	—
(c)	10Dq	17088	27986	874	0.84	+159	12.17	—	—	—	—	1.33	—	—
(d)	10Dq	16987	27527	840	0.81	−250	12.66	—	—	—	—	1.58	—	—
							[$Ni(C_{11}H_9ON_3S)_2$]							
Experimental	11364	16666	26315	—	—	—	—	—	1.47	2.32	1.28	—	38.95	3.14
(a)	10Dq	fitted	25918	566	0.54	−402	20.08	88.4	—	—	—	3.83	—	—
(b)	10Dq	16928	fitted	610	0.59	+262	18.63	—	—	—	—	3.42	—	—
(c)	10Dq	16831	26156	593	0.57	−159	19.16	—	—	—	—	3.58	—	—
(d)	10Dq	17247	26895	670	0.64	+580	16.96	—	—	—	—	3.00	—	—
							[$Ni(C_{18}H_{12}O_2N_2S_2)Cl_2$]							
Experimental	10869	16129	25000	—	—	—	—	—	1.48	2.30	1.22	—	37.27	3.16
(a)	10Dq	fitted	25071	573	0.55	+71	18.97	79	—	—	—	3.75	—	—
(b)	10Dq	16085	fitted	565	0.54	−44	19.24	—	—	—	—	3.88	—	—
(c)	10Dq	16103	25024	568	0.55	+24	19.14	—	—	—	—	3.75	—	—
(d)	10Dq	16008	24879	552	0.53	−121	19.69	—	—	—	—	3.92	—	—

TABLE 4—SELECTED INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF COBALT(II) AND NICKEL(II) SCHIFF BASE COMPLEXES

Compd.	ν_{COOH}	$\nu_{C=O}$	$\nu_{CH=N}$	$\nu_{as(COO)}$	$\nu_{s(COO)}$	ν_{C-S-C}	ν_{M-N}	ν_{M-O}	ν_{M-S}	ν_{M-Cl}
$C_{18}H_9O_3NS$	2610 m	1720 m	1590 s	1620 m	1390 m	1220 s	—	—	—	—
[$Co(C_{18}H_9O_3NS)(H_2O)_2$]	—	1668 s	1580 s	1500 b	1395 m	1235 s	580 b	465 w	370 vw	—
[$Ni(C_{18}H_9O_3NS)(H_2O)_2$]	—	1680 s	1585 m	1540 w	1395 w	1260 s	530 b	485 w	322 w	—
$C_{18}H_{11}ONS$	—	1660 s	1610 m	—	—	1240 m	—	—	—	—
[$Co(C_{18}H_{11}ONS)_2$]	—	1635 m	1580 m	—	—	1262 w	530 w	435 w	360 vw	—
[$Ni(C_{18}H_{11}ONS)_2$]	—	1715 m	1630 m	—	—	1280 m	540 w	425 w	340 w	—
$C_{11}H_9ON_3S$	—	1660 s	1610 w	—	—	1225 m	—	—	—	—
[$Co(C_{11}H_9ON_3S)_2$]	—	1650 m	1590 s	—	—	1155 m	535 w	425 w	338 w	—
[$Ni(C_{11}H_9ON_3S)_2$]	—	1640 m	1585 s	—	—	1260 s	525 b	440 w	355 w	—
$C_{18}H_{12}O_2N_2S_2$	—	1660 m	1630 m	—	—	1265 w	—	—	—	—
[$Co(C_{18}H_{12}O_2N_2S_2)Cl_2$]	—	1620 s	1570 m	—	—	1262 s	580 m	460 w	—	265 m
[$Ni(C_{18}H_{12}O_2N_2S_2)Cl_2$]	—	1640 w	1565 w	—	—	1260 m	560 m	482 w	—	270 w

s = strong, m = medium, w = weak, b = broad, vw = very weak.

cm^{-1} (C=O) shift to lower frequency in the complexes showing coordination of metal ion through these groups. Thiophene stretching frequency in the region 1220-1265 cm^{-1} shows a shift of 15-45 cm^{-1} indicating its involvement in chelation except for the complexes [$Co(C_{18}H_{12}O_2N_2S)Cl_2$] and [$Ni(C_{18}H_{12}O_2N_2S_2)Cl_2$]. The frequency 2610 cm^{-1} (COOH) in the ligand $C_{18}H_9O_3NS$ disappears in the complexes. The symmetric and asymmetric stretching band on complexation also get shifted indicating the involvement of carboxylic group in bonding[21].

Appearance of new bands at 525-580, 425-485 and 322-370 cm^{-1} may be assigned to (M−N), (M−O) and (M−S) stretching frequencies, respectively supporting chelation through these groups. In the complexes [$Co(C_{18}H_{12}O_2N_2S_2)Cl_2$] and [$Ni(C_{18}H_{12}O_2N_2S_2)Cl_2$] the bands at 265 and 270 cm^{-1}, respectively are assigned to M−Cl stretching mode[22].

References

1. E. M. HODNETT, C. H. MOORE and F. A. FRENCH, *J. Med. Chem.*, 1971, **14**, 1121.
2. A. CHIRIOC, O. DRAGOMIR, F. MOTOC and I. MOTOC, *Ser. Chim.*, 1979, **1**, 3.
3. M. AKBARALI, S. E. LIVINGSTONE, *Coord. Chem. Rev.*, 1974, **13**, 101.
4. D. T. CHAUDHARY and S. S. SABNIS, *Bull. Haffkine Inst.*, 1976, **4**, 85.
5. E. UEDA, N. MATSUOKA and Y. SHIMURA, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 136.
6. R. PASTOREK and F. BREZINA, *Z. Chem.*, 1981, **21**, 39.

7. B. Chiswell, J. P. Crawford and E. J. O'. Reilly, *Inorg. Chim. Acta*, 1980, **40**, 223.
8. V. P. Kurbatov, T. V. Torgova, O. A. Osipov and N. A. Belonog, *Koord. Khim.*, 1981, **7**, 207.
9. F. Kipnis and J. Ornfelt, *J. Am. Chem. Soc.*, 1946, **68**, 2734.
10. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", Longmans, London 3rd ed., 1969.
11. W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
12. B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 1964, **6**, 197.
13. N. A. Patel, J. R. Shah and R. P. Patel, *Indian J. Chem., Sect. A*, 1980, **19**, 286.
14. E. Konig, *Inorg. Chem.*, 1971, **10**, 2632.
15. E. Konig, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1173, 2877.
16. H. S. Verma, A. Pal, R. C. Saxena and A. K. Katiyar, *J. Indian Chem. Soc.*, 1983, **60**, 84.
17. A. B. P. Lever and D. Ogden, *J. Chem. Soc.* (*A*), 1967, 2041.
18. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.
19. E. Konig, *Struct. Bonding* (*Berlin*), 1971, **9**, 175.
20. A. B. P. Lever, *Adv. Chem.*, 1966, **62**, 485.
21. B. Singh, V. Banerjie, B. V. Agarwala and A. K. Dey, *J. Indian Chem. Soc.*, 1980, **57**, 36.
22. G. Panticelli, *J. Inorg. Nucl. Chem.*, 1977, **39**, 45.

A Study in the Complex Formation of Thiodiacetic, Thiodipropionic, Dithiodiacetic, Iminodiacetic and Oxydiacetic Acids with Nickel and Copper Ions

S. N. DUBEY,* R. K. BAWEJA and D. M. PURI

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

Manuscript received 3 April 1983, revised 24 January 1984, accepted 17 June 1984

A survey of the literature[1-4] revealed that no effort appears to have been made to determine the thermodynamic stability constants of the complexes formed by Ni^{II} and Cu^{II} ions with thiodiacetic acid (TDAA), thiodipropionic acid (TDPA), dithiodiacetic acid (DTDAA), iminodiacetic acid (IDAA) and oxydiacetic acid (ODAA). In view of the above and also the results reported[5-7] by us on the chelation abilities of the above mentioned ligands, it was considered of interest to study Ni^{II} and Cu^{II} systems potentiometrically. The thermodynamic stability constants of Ni^{II} and Cu^{II} complexes were obtained by extrapolating the determined stability constants at various ionic strengths (0.1, 0.2 and 0.3 *M*, 25°) to zero ionic strength. The thermodynamic functions (ΔG, ΔH and ΔS) were calculated at 0.1 *M*. The titration technique adopted was that of Calvin and Wilson as modified by Irving and Rossotti[8-10].

Experimental

The solutions of TDAA, TDPA and DTDAA (Evan's), IDAA (Sigma), ODAA (John Backer), nickel sulphate ($NiSO_4.H_2O$, A.R.) and copper sulphate ($CuSO_4.5H_2O$, A.R.) were prepared in double distilled water. Perchloric acid (0.04 *M*) solution was prepared from the stock solution by dilution with double distilled water and standardised against standard NaOH solution. Other chemicals used were of A.R. grade. The stock solutions of nickel sulphate and copper sulphate were standardised gravimetrically.

A Philips (PR 9405 *M*) *p*H meter with glass and calomel electrodes assembly was used to measure the *p*H. The instrument was calibrated at *p*H 4.0 and 9.2. The experimental details were the same as reported earlier[11]. An appropriate quantity of sodium perchlorate (2.0 *M*) was added to maintain the desired ionic concentrations at 0.1, 0.2 and 0.3 *M*.

Results and Discussion

The *p*H range investigated for Ni^{II}-TDAA, Ni^{II}-TDPA, Ni^{II}-DTDAA, Ni^{II}-IDAA, Ni^{II}-ODAA, Cu^{II}-TDAA, Cu^{II}-TDPA, Cu^{II}-IDAA and Cu^{II}-ODAA systems were 2.45-4.80, 3.60-4.70, 3.50-4.70, 2.80-6.80, 3.40-5.20, 2.40-5.20, 3.20-4.40, 2.40-7.40 and 2.60-3.20, respectively.

The proton-ligand stability constants of TDAA, TDPA, DTDAA, IDAA and ODAA, and the stepwise formation constants of their chelates with Ni^{II} and Cu^{II} were determined at 25$\pm$0.5, 35$\pm$0.5 and 45$\pm$0.5° using Irving-Rossotti technique and the values were further refined using the computational techniques[12,13], (*i*) curvefitting method and (*ii*) pointwise calculation method. The protonation constant values of TDAA, TDPA, DTDAA, IDAA and ODAA determined at different ionic concentrations and temperatures are the same as reported earlier[6]. The stepwise formation constants of Ni^{II} and Cu^{II} chelates are given in Table 1.

In Ni^{II}-TDPA, Ni^{II}-DTDAA, Ni^{II}-ODAA, Cu^{II}-TDPA and Cu^{II}-ODAA systems, the $\bar{n}$ values varied between 0.1 and 0.9, thereby indicating the formation of only 1 : 1 complex. In Ni^{II}-TDAA, Ni^{II}-IDAA, Cu^{II}-TDAA and Cu^{II}-IDAA systems, $\bar{n}$ values varied between 0.2 and 1.9, indicating the formation of 1 : 1 and 1 : 2 complexes. Cu^{II}-DTDAA systems could not be studied as precipitation starts from the very beginning.

It is evident from Table 1 that metal-ligand formation constants increase with increase in ionic strength and decrease with increase in temperature. The thermodynamic formation constants were evaluated by extrapolating the concentration formation constants to zero ionic strength and the values are given in Table 1. The general trend in the overall thermodynamic stabilities indicates that the Cu^{II} complexes are more stable as compared to the Ni^{II} complexes.

The thermodynamic functions ΔG, ΔH and ΔS were calculated using the standard equations[14] and the values are given in Table 2. Chelates of Ni^{II} and Cu^{II} with the ligands are formed spontaneously as revealed by the negative ΔG values. The overall changes in ΔH and ΔS values indicate that

TABLE 1—FORMATION CONSTANTS OF Ni^{II} AND Cu^{II} COMPLEXES

System	Formation constants	Ionic strength 0.1, Temp. 25°	0.2, Temp. 25°	0.3, Temp. 25°	0.1, 35°	0.1, 45°	0.0, 25°
Ni^{II}-TDAA	log K_1	4.26	4.49	4.66	4.26	4.23	4.07
	log K_2	2.88	2.99	3.20	2.78	2.75	2.64
Ni^{II}-TDPA	log K_1	3.36	3.47	3.56	3.38	3.31	3.28
Ni^{II}-DTDAA	log K_1	2.84	2.89	2.91	2.88	2.78	2.81
Ni^{II}-IDAA	log K_1	8.22	8.27	8.31	8.21	8.18	8.17
	log K_2	6.08	6.05	6.10	5.96	5.92	6.00
Ni^{II}-ODAA	log K_1	2.74	2.77	2.81	2.72	2.69	2.70
Cu^{II}-TDAA	log K_1	4.63	4.66	4.69	4.61	4.60	4.60
	log K_2	2.81	2.83	2.84	2.81	2.77	2.79
Cu^{II}-TDPA	log K_1	3.96	4.01	4.05	3.93	3.92	3.92
Cu^{II}-IDAA	log K_1	8.63	8.68	8.72	8.59	8.55	8.58
	log K_2	5.80	5.88	5.94	5.78	5.76	5.73
Cu^{II}-ODAA	log K_1	3.95	3.99	4.03	3.93	3.89	3.91

TABLE 2—THERMODYNAMIC PARAMETERS OF Ni^{II} AND Cu^{II} COMPLEXES

μ=0.1 M

System	$-\Delta G$ kcal mol^{-1}	$-\Delta H$ kcal mol^{-1}	ΔS cal deg^{-1} mol^{-1}
Ni^{II}-TDAA	9.67	2.85	22.18
Ni^{II}-TDPA	4.58	1.34	10.51
Ni^{II}-DTDAA	3.87	1.66	7.17
Ni^{II}-IDAA	19.44	3.25	52.52
Ni^{II}-ODAA	3.74	1.72	6.55
Cu^{II}-TDAA	10.16	3.32	22.16
Cu^{II}-TDPA	5.40	1.04	14.15
Cu^{II}-IDAA	19.68	3.73	50.46
Cu^{II}-ODAA	5.39	1.90	11.82

the complexes are both enthalpy and entropy stabilized. The relatively smaller values of ΔH in comparison to that of ΔS indicate that entropy is the principal driving force for the complex formation in aqueous solution.

Acknowledgement

The authors are thankful to Prof. V. Yatirajam, Chairman, Chemistry Department, Kurukshetra University for facilities.

References

1. M. YASADA, K. YAMASAKI and H. OHTAKI, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 1067.
2. K. S. BAJAN and A. E. MARTELL, *J. Inorg. Nucl. Chem.*, 1964, **26**, 789.
3. S. CHABEREK and A. E MARTELL, *J. Am. Chem. Soc.*, 1952, **74**, 5052.
4. G. SCHWARZENBACH, H. ACKERMANN and P. RUCKSTUHL, *Helv. Chim. Acta*, 1949, **32**, 1175.
5. S. N. DUBEY, R. K. BAWEJA and D. M. PURI, *J. Indian Chem. Soc.*, 1980, **57**, 244.
6. S. N. DUBEY, R. K. BAWEJA and D. M. PURI, *J. Indian Chem. Soc.*, 1982, **59**, 1133.
7. S. N. DUBEY, R. K. BAWEJA and D. M. PURI, *Indian J. Chem., Sect. A*, 1983, **22**, 450.
8. J. BJERRUM, "Metal Ammine Formation in Aqueous Solution", P. Haase and Sons, Copenhagen, 1941.
9. M. CALVIN and K. W. WILSON, *J. Am. Chem. Soc.*, 1945, **67**, 2003.
10. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
11. S. ARORA, H. L. KALRA, S. N. DUBEY and D. M. PURI, *J. Indian Chem. Soc.*, 1978, **55**, 445.
12. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
13. S. N. DUBEY and R. C. MEHROTRA, *Indian J. Chem.*, 1967, **5**, 327.
14. K. B. YATSIMIRSKII and V. P. VASIL'EV, "Instability Constants of Complex Compounds", Pergamon Press, London, 1960, p. 59.

Studies on L-2-Aminomercaptopropionic Acid Metal Complex Equilibria

SALEEM IFTEKHAR and K. P. DUBEY

Department of Chemistry, University of Kashmir, Srinagar-190 006

Manuscript received 22 February 1983, revised 7 October 1983, accepted 17 June 1984

OUT of sulphur containing amino acids, the investigation on the complexes of D-penicillamine and L-2-aminomercaptopropionic acid are reported in literature[1]. In this note we report our results on stepwise stability constants of L-2-aminomercaptopropionic acid with Be^{II}, La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Au^{III}, Zr^{IV}, Pt^{IV}, Th^{IV} and $U^{II}O_2$. We have evaluated thermodynamic parameters from the values obtained on stability constants using temperature coefficient and Gibbs-Helmholtz equation[2].

Experimental

L-2-Aminomercaptopropionic acid (Eastern Organic Chemicals) was assayed by iodometry and by iron catalysed oxidation with oxygen and found to contain 95% SH group[3]. Throughout the investigation, standard solution of L-2-aminomercaptopropionic acid was stored under N_2 and discarded after 1 day. Assays of 2 days' old solutions stored under N_2 showed that the percentage of SH group lowered to 92%.

The *p*H-titration of L-2-aminomercaptopropionic acid with proton and various metal ions was conducted at 0.1 *M* ionic strength using KNO_3 by Bjerrum and Calvin *p*H titration technique as modified by Irving and Rassotti[4-5]. All the experiments were performed in N_2 atmosphere. The following reaction mixtures were prepared to study metal ion – L-2-aminomercaptopropionic acid complex equilibria: (i) KNO_3 (1.0 *M*) 5.0 ml+HNO_3 (0.05 *M*) 5.0 ml, (ii) KNO_3 (1.0 *M*) 5.0 ml+HNO_3 (0.05 *M*) 5.0 ml+L-2-aminomercaptopropionic acid (0.01 *M*) 10.0 ml, (iii) KNO_3 (1.0 *M*) 5.0 ml+HNO_3 (0.05 *M*) 5.0 ml+L-2-aminomercaptopropionic acid (0.01 *M*) 10.0 ml+metal ion (0.01 *M*) 2.0 ml. The total volume of reaction mixture was raised to 50.0 ml by adding distilled water. Reaction mixture was titrated with alkali. Before titration, reaction mixtures were kept in a thermostat to attain the desired temperature.

Results and Discussion

From the titration curves, it has been observed that in the lower *p*H range (3.0-4.5), L-2-aminomercaptopropionic acid shows higher values of *p*H as compared to acid curve. The ligand diverges from the acid curve on further addition of alkali. It has generally been observed that the complex curve overlaps with ligand in the lower *p*H range but diverges towards right at higher *p*H, indicating the release of proton due to complex formation. The formation of complex is also supported by the fact that the solutions undergo marked change in colour. Further rise in *p*H leads to precipitation of hydrolysed species. From the differences in the curves n̄H and n̄ were evaluated. Protonation constant values were evaluated using Bjerrums half n̄ method and Speakman's method[6]. The same method was applied for evaluating the stepwise stability constant of metal complexes from the n̄/*p*L data. The results obtained on stability constants and thermodynamic parameters are given in Table 1. The measured protonation constant of L-2-aminomercaptopropionic acid are in good agreement with the reported values[7]. The gradual deprotonation of L-2-aminomercaptopropionic acid by addition of alkali leads to the following progressive formation of metal ion : L-2-aminomercaptopropionic acid complexes.

$$[M]^{n+} + [\text{L-cyst}]^{2-} \rightarrow [M(\text{L-cyst})]^{n^+ + 2^-}$$

$$[M(\text{L-cyst})]^{n^+ + 2^-} + [\text{L-cyst}]^{2-} \rightarrow [M(\text{L-cyst})_2]^{n^+ + 4^-}$$

$$[M(\text{L-cyst})_2]^{n^+ + 4^-} + [\text{L-cyst}]^{2-} \rightarrow [M(\text{L-cyst})_3]^{n^+ + 6^-}$$

$$[M(\text{L-cyst})_3]^{n^+ + 6^-} + [\text{L-cyst}]^{2-} \rightarrow [M(\text{L-cyst})_4]^{n^+ + 8^-}$$

The order of stability constants of metal complexes is as follows: $Au^{III} > Pt^{IV} > Th^{IV} > U^{II}O_2 > Ce^{III} > Nd^{III} > Pr^{III} > Zr^{IV} > La^{III} > Be^{II}$.

Gold(III) and platinum(IV) have very high B-class character, therefore, their complexes exhibit highest stabilities. From thorium(IV) onwards the B-class character decreases and the stability constants also decrease, the lowest stability constants being exhibitted by lanthanum(III) and beryllium(II) complexes as these two metal ions have typical A-class character.

TABLE 1—STABILITY CONSTANT AND FREE ENERGY CHANGE VALUES OF M^{n+} : L-2-AMINOMERCAPTOPROPIONIC ACID SYSTEM

Cation	Temp. 15°/(30°)			$-\Delta F°$ kcal mol^{-1}
	log K_1	log K_2	log β_n	
Be^{II}	12.60 (12.35)	7.50 (7.40)	20.00 (19.75)	16.46 (17.11)
La^{III}	13.35 (13.25)	5.30 (5.20)	18.65 (18.45)	17.58 (18.36)
Ce^{III}	13.50 (13.40)	7.00 (6.90)	20.50 (20.30)	17.77 (18.57)
Pr^{III}	13.40 (13.30)	5.25 (5.15)	18.65 (18.45)	17.64 (18.43)
Nd^{III}	13.45 (13.35)	5.30 (5.20)	18.75 (18.55)	17.71 (18.50)
Au^{III}	14.85 (14.65)	—	14.85 (14.65)	19.55 (20.30)
Pt^{IV}	13.40 (13.35)	5.25 (5.15)	18.65 (18.50)	17.64 (18.50)
Zr^{IV}	14.40 (13.15)	—	14.40 (14.15)	18.96 (19.61)
Th^{IV}	14.30 (14.05)	—	14.30 (14.05)	18.83 (19.47)
$U^{II}O_2$	13.80 (13.65)	8.70 (8.55)	22.50 (22.20)	18.17 (18.91)

Accuracy of all values are ±0.02. Protonation constant values of L-2-aminomercaptopropionic acid at 15° and 30° are log K_1^H=10.45 (10.35) ; log K_2^H=8.15 (8.10) ; log B^H=18.60 (18.45), respectively.

References

1. J. J. CHRISTENSEN and R. M. IZAT, "Handbook of Metal Ligand Heat and Related Thermodynamic Quantities", Marcel Dekker, New York, 1972.
2. K. B. YATSIMIRSKI and V. P. VASIL'ev, "Instability Constants of Complex Compounds", Pergamon Press, New York, 1960.
3. T. F. LAVINE, *J. Biol. Chem.*, 1935, **109**, 141.
4. J. BJERRUM, "Metal Ammine Formation in Aqueous Solution", P. Haase and Sons, Copenhagen, 1941.
5. H. IRVING and J. S. RASSOTTI, *J. Chem. Soc.*, **1954**, **2904**.
6. J. C. SPEAKMAN, *J. Chem. Soc.*, 1940, 855.
7. A. E. MARTELL and R. M. SMITH, "Critical Stability Constants, Amino Acids", Plenium Press, N. Y.

Tetrakispyridine-2-carboxylatoniobium(IV) and Trispyridine-2-carboxylatooxoniobium(V)

A. V. SAHA and SUBHA SEN

Department of Chemistry, University College of Science, Calcutta-700 009

Manuscript received 14 December 1982, revised 29 July 1983, accepted 21 July 1984

NO niobium complex containing pyridine-2-carboxylate anion as the ligand is reported in the literature. This communication describes the preparation and properties of tetrakispyridine-2-carboxylatoniobium(IV) as a monomeric violet-red complex and its colourless oxidation product, tris pyridine-2-carboxylatooxoniobium(V). The niobium(IV) complex is interesting[1] because of its unquenched magnetic moment corresponding to d^1 configuration free from Nb-Nb interaction.

Experimental

Reagents, apparatus and analysis : Potassium disulphatoniobate(III) was prepared by the reported method[2] using niobium(V) oxide (Fluka, 99.8%). All other reagents were of appropriate purity. Nitrogen gas was purified by washing with acidified Cr^{II} solution. Ir spectra were recorded on a Beckman IR 20 in KBr pellets, the electronic spectra on a Hilger UVISPEK and the conductance values were measured by a Philips' RCL bridge. Molecular weight determination was carried out in camphor by Rast's method. Magentic susceptibility was measured with a Gouy balance. Niobium was determined as Nb_2O_5 by ignition and C, H and N analysed by micro combustion.

Tetrakispyridine-2-carboxylatoniobium(IV), $Nb(C_6H_4NO_2)_4$: 200 mg of freshly prepared potassium disulphatoniobate(III) tetrahydrate was freed from sulphuric acid by washing with ethanol. The solid was allowed to react with 400 mg of pyridine-2-carboxylic acid hydrochloride in 5 ml water. The deep red solution was immediately extracted with 125 ml chloroform in portions and the extract was evaporated in a rotary vacuum evaporator. The experiment upto this stage was carried out in nitrogen atmosphere. The dry material is sufficiently stable to permit further experiments in presence of air. The product obtained was extracted with 100 ml dry benzene to remove any oxidised $NbO(C_6H_4NO_2)_3$. The benzene solution was then evaporated to afford violet-red needles and dried. The powdered solid was heated to 150° in a stream of dry oxygen-free nitrogen when free ligand present as impurity sublimed off to yield the purified product (250 mg) (Found : C, 49.5 ; H, 2.28 ; N, 9.7 ; Nb, 16.6%. $Nb(C_6H_4NO_2)_4$: Calcd. C, 49.8 ; H, 2.75 ; N, 9.6 ; Nb, 16.0%).

Trispyridine-2-carboxylatooxoniobium(V), $NbO(C_6H_4NO_2)_3$: 100 mg of tetrakispyridine-2-carboxylatoniobium(IV) in 10 ml of chloroform was oxidised by passing moist chlorine gas until decolourisation of the solution was complete. The precipitated pyridine-2-carboxylic acid hydrochloride was removed and the solution evaporated. The dry mass was washed with benzene to yield the product (75 mg) (Found : N, 9.0 ; Nb, 19.6%. $NbO(C_6H_4NO_2)_3$: Calcd. N, 8.9 ; Nb, 19.6%).

Results and Discussion

$Nb(C_6H_4NO_2)_4$ is a shining crystalline solid stable in a dry inert atmosphere. Moist air slowly converts it to the tris compound. The complex is freely soluble in all common organic solvents and is decomposed by water. The oxidation number of niobium, determined by oxidising known quantities of the tetrakis compound with standard iodine solution, is 4.00 ± 0.05. It shows that during the formation of this complex in aqueous medium the Nb^{III} in the starting compound was oxidised to Nb^{IV}. To prove that the compound is not a mixed valence polymer[3], its molecular weight was determined and the mean observed value was 590 *vis-a-vis* the required value of 581 for a monomeric unit. The molecular conductance value, 0.84 Ω^{-1} cm^2 in DMSO, proves it to be a non-electrolyte. These data more or less establish that the complex is really a tetrakis derivative which is further proved by its μ_{eff} value 1.53 B.M. at room temperature, being the same as that of tetrakis niobium(IV) complexes[4-7].

$NbO(C_6H_4NO_2)_3$ is the product of controlled oxidation of the tetravalent complex, the control being really that of the water content. This is so susceptible to hydrolytic attack that the pentavalent complex can never be obtained in aqueous environment.

$$2Nb^{IV}(C_6H_4NO_2)_4 + Cl_2 + 2H_2O \rightarrow 2Nb^VO(C_6H_4NO_2)_3 + 2C_6H_5NO_2.HCl$$

The electronic spectra of both the complexes in chloroform show 37.7 kK band for the ligand transition. The d-d band for $Nb^{IV}(C_6H_4NO_2)_4$ (d^1) is observed at 19.3 kK ($\epsilon = 3750$) obviously gaining intensity owing to charge transfer[6,8]. The ir bands[9-11] are observed at 315 (Nb–N) and 450 cm^{-1} (Nb–O) for $Nb(C_6H_4NO_2)_4$. The Nb=O band in $NbO(C_6H_4NO_2)_3$ can be easily identified[12,13] at 920 cm^{-1} which is obviously absent in tetrakis complex. The C–O band of the ligand is observed at 1665 cm^{-1} for the Nb^{IV} complex and at 1690 cm^{-1} for the Nb^V complex, while in $K[C_6H_4NO_2]$ the band is observed at 1610 cm^{-1} and in the free acid at 1700 cm^{-1}. The values are in conformity[14] with the expectations.

Acknowledgement

The authors thank Dr. B. K. Sen of this Department and Swami Muktirupananda, Principal, R. K. M. Residential College, Narendrapur, for encouragement.

References

1. D. A. Miller and R. D. Bereman, *Coord. Chem. Rev.*, 1972, **9**, 107.
2. R. N. Gupta and B. K. Sen, *Z. Anorg. Allg. Chem.*, 1973, **398**, 812.
3. A. V. Saha, R. K. Maiti, R. N. Gupta and B. K. Sen, *Indian J. Chem., Sect. A*, 1977, **15**, 43.
4. D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc.*, 1969, 1152.
5. J. B. Hamilton and R. E. McCarley, *Inorg. Chem.*, 1970, **9**, 1339.
6. R. L. Deutscher and D. L. Kepart, *Chem. Commun.*, 1969, **3**, 121.
7. R. J. H. Clark, D. L. Kepart, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2865.
8. R. L. Deutscher and D. L. Kepart, *Inorg. Chim. Acta*, 1970, **4**, 645.
9. R. J. H. Clark and C. S. Williums, *Inorg. Chem.*, 1965, **4**, 350.
10. J. Takemoto, *Inorg. Chem.*, 1973, **12**, 949.
11. R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, 1965, **42**, 2590.
12. R. G. Charles, H. Freiser, R. Friedel, L. E. Hilliard and W. D. Johnston, *Spectrochim. Acta*, 1956, **8**, 1.
13. J. P. Phillips and J. F. Deye, *Anal. Chim. Acta*, 1957, **17**, 233.
14. R. E. Sievers and J. C. Bailar, *Inorg. Chem.*, 1962, **1**, 174.

Study of Lead(II) Chelates of Penicillins

PURUSHOTTAM B. CHAKRAWARTI, (MISS) C. P. TIWARI, ANURADHA TIWARI and H. N. SHARMA

Chemical Laboratories, M. L. B College, Bhopal-462 005

Manuscript received 20 May 1982, revised 21 January 1984, accepted 17 June 1984

LEAD salts have been shown to induce renal adenomas and renal adenocarcinomas in rodents following administration by dietary and parenteral routes[1-3]. In addition, carcinomas of the testis and adenomas of the adrenal, thiroid, pituitary, postate and lungs following chronic dietary administration of lead acetate to rats have been reported[4]. The carcinogenicity of tetraethyl lead has been tested following subcutaneous infection into neonatal Swiss mice[5]. Recent study in metal carcinogenesis in experimental animals has shown prohibition of tumours in the control rats receiving penicillin solutions[6]. Since cancer formation and its inhibition both are supposed to involve chelation[7], the value of formation and thermodynamic constants of metal complexes of these drugs will give important information in the understanding of their biological activity.

Hence, in the present note we report the thermodynamic parameters and characterisation of the isolated complexes of Pb^{II} with penicillins, V and G (PV and PG).

Experimental

All the chemicals used were of high purity, while the experimental details remain the same as in our previous communications[8].

Stoichiometry of the various species formed was determined using conductometric titrations and the stability constants were computed by Bjerrum-Calvin *p*H titration technique as adopted by Irving and Rossotti[9].

Thermodynamic parameters—the values of the changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying the metal ligand complex forming reactions have been calculated at various temperatures using the relations

$$\Delta G = -RT \log k$$

$$\Delta H = \frac{4.57 \, (d \log k)}{d \, (1/T)}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

Equimolar solution of the metal and the ligand (penicillin G or V) in 1 : 2 ratio in 80% acetone-water (v/v) solution was refluxed for 4 h. The solution was then concentrated to one-fifth the original volume on a water bath. The complex was separated by vacuum filtration, washed with ether and dried under vacuum.

The composition of the complexes was ascertained by elemental analyses and the presence of the lattice water was estimated from the difference in the weight obtained on heating them to 110°. The results are recorded in Table 1. Ir spectra (KBr) were recorded on Perkin-Elmer Model 237 spectrophotometer.

TABLE 1—ANALYTICAL DATA OF Pb^{II} CHELATES

PG = $C_{16}H_{17}O_4N_2S$
PV = $C_{16}H_{17}O_5N_2S$

Compd.	Analysis % : Found/(Calcd.)					
	C	H	N	S	M	H_2O
PG chelate	32.10 (31.70)	3.81 (3.74)	6.33 (6.41)	7.41 (7.33)	23.11 (22.89)	3.40 (3.52)
PV chelate	31.30 (30.62)	3.70 (3.60)	6.23 (6.19)	7.12 (7.07)	22.15 (22.89)	3.47 (3.40)

Results and Discussion

The conductometric titrations show formation of ML and ML_2 complexes between Pb^{II} and penicillin G and V, while *p*H titrations indicate removal of one proton during complexation of each molecule. The *p*H titrations did not indicate formation of 1 : 3 complex in these systems. All attempts to trace possibility of complexation of more than two molecules of the ligand gave negative results. This may be due to the steric hindrance caused by the bulky molecules of PG and PV. Thus, the complex formation may be as follows :

$$M^{2+} + HL = ML^{+} + H^{+} \quad (1)$$

$$ML^{+} + HL = ML_2 + H^{+} \quad (2)$$

where HL = penicillin G or V.

An analysis of the formation curves (Fig. 1) indicates that addition of PV follows the mechanism of simultaneous addition and the two species co-exist in solution. The addition of PG on the other hand follows the mechanism of independent addition.

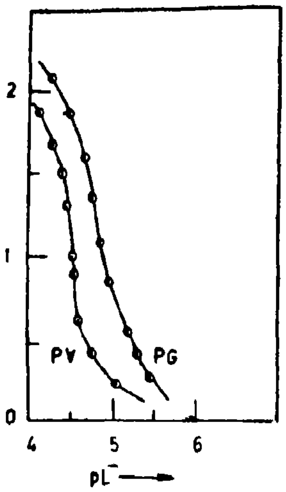


Fig. 1. Formation curves at 30°.

The values of formation constants and free energy change (Table 2) show that the penicillin G complex is more stable than that with penicillin V. This is in accordance with the base strengths of the two ligands (log k_1^H values for penicillin G and penicillin V, at 30° and 0.1 *M* ionic strength, being 4.77 and 3.98, respectively)[8].

The perusal of the values of the thermodynamic parameters (Table 2) clearly indicates that the reactions of these penicillins with Pb^{II} are enthalpy characterised reactions, since the values of entropy change are negative. The high values of negative enthalpy change indicate considerable degree of covalence in metal to ligand bond[11] which presumably involve metal to nitrogen bonding. Further, the value of ΔG for each stage is less negative than those of ΔH and each substitution therefore has negative ΔS (Table 1). The negative value of ΔS was predicted also to be due to the effect of solvent[12].

The analytical data indicate the general formula for the complexes to be $ML_2.2H_2O$. The ratio of the successive formation constants, k_1/k_2, are positive and show no abrupt or unusual changes, indicating the normal stoichiometry for the complexes studied. Further, with the use of very dilute solution ($1\times10^{-4}M$) of the metal possibility of the formation of polynuclear complexes may be ruled out.

The ir spectra of the complexes show that while most of the bands remain unchanged on complexation, there is a considerable shift in the frequencies of the carbonyl group and a slight deviation in that of the tertiary nitrogen of the β-lactam thiazolidine ring. Whereas the band due to tertiary nitrogen of the β-lactam thiazolidine at 1770 cm^{-1} varies

TABLE 2—STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF Pb^{II} CHELATES

μ=0.1 *M* ($NaClO_4$)

	Temp.	Ligand log β_1	Pb^{II} Chelate log k_1	log k_2	log β_2	Method*
Penicillin G**	20°	4.89	5.45	4.85	10.30	a
			5.44	4.95	10.40	b
	30°	4.77	5.34	4.70	10.04	a
			5.20	4.70	9.90	b
	40°	4.37	4.96	4.45	9.41	a
			4.95	4.39	9.34	b
Penicillin V**	20°	4.17	4.88	4.55	9.48	a
			5.02	4.56	9.56	b
	30°	3.98	4.60	4.32	8.92	a
			4.68	4.28	8.96	b
	40°	3.49	4.32	4.03	8.35	a
			4.37	3.90	8.27	b
			$-\Delta G_1$	$-\Delta G_2$ kcal mol^{-1}	$-\Delta G_2$ (overall)	Temp. °C
Penicillin V			6.81	6.14	12.92	20
			6.54	5.99	12.58	30
			6.24	5.70	12.53	40
Penicillin G			6.85	6.61	13.96	20
			6.84	6.57	13.41	30
			6.50	6.37	12.87	40
			$-\Delta H_1$	$-\Delta H_2$ kcl mol^{-1}	$-\Delta H_2$ (overall)	
Penicillin V			18.05	18.00	25.65	30
Penicillin G			13.71	13.25	21.94	30
			$-\Delta S_1$	$-\Delta S_2$ cal $k^{-1}mol^{-1}$	$-\Delta S_2$ (overall)	
Penicillin V			37.97	39.64	43.30	30
Penicillin G			25.96	22.06	26.32	30

* a=Half n̄ method ; b=Least square method.
**Ref. 8.

slightly, the band due to antisymmetric stretching of $-C\langle^{O}_{O}\rangle^{\ominus}$ in potassium salts of penicillin G or V shifts from ~1600 to ~1700 cm^{-1}. This clearly indicates that the penicillin molecules are attached to the metal by chelation (forming a five membered ring) through the carboxyl group (replacing the hydrogen) and the tertiary nitrogen of the β-lactam with donation of the lone pair of electrons on it (Fig. 2).

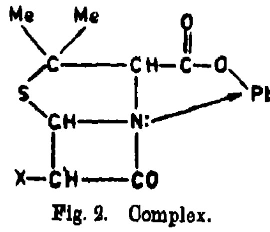


Fig. 2. Complex.

With the attachment of two molecules of the ligand (PG or PV) only four coordination sites are filled, the remaining two coordination positions in the octahedral geometry of the complexes being occupied with two water molecules. This finds confirmation[13,14] in the presence of bands near

3200, 1600 and 800 cm^{-1}. Low values of pKa for these drugs ensure that they are almost entirely in the form of the complex forming species (the anion) at the physiological pH 7.3. Formation of only ML and ML_2 complexes indicates that the coordination number six for the metal ion is not attained. This may favour the attachment of the drug-chelate with the tissue, thus binding these drugs with the nucleic acid and affecting the structure and functions of nucleic acids, resulting in beneficial effects.

References

1. E. BOYLAND, C. E. DUKES, P. L. GROVER and C. B. V. MITCHLEY, *Br. J. Cancer*, 1962, **16**, 283.
2. F. J. C. ROE, E. BOYLAND, C. S. DUKES and C. B. V. MITCHLEY, *Br. J. Cancer*, 1965, **19**, 860.
3. G. J. VAN ESCH, H. VAN GENDEREN and H. H. VINK, *Br. J. Cancer*, 1962, **16**, 289.
4. B. ZAWIRSKA and K. MEDRAS, *Zentbl. Allg. Path. Anat.*, 1968, 1.
5. S. S. EPSTEIN and N. MANTEL, *Experientia*, 1968, **24**, 580.
6. F. W. SUNDERMAN, *Food Cosmet. Toxicol.*, 1971, **9**, 105.
7. A. FRUST, "Chemistry of Chelation in Cancer", Thomas Springfield, 1963.
8. A. TIWARI, H. N. SHARMA and P. B. CHAKRAWARTI, *Indian J. Chem., Sect. A*, 1981, **19**, 83; A. TIWARI, P. B. CHAKRAWARTI and H. N. SHARMA, *J. Indian Chem. Soc.*, 1979, **56**, 533; A. TIWARI, H. N. SHARMA and P. B CHAKRAWARTI, *Proc. Natl. Acad. Sci., India, Sect. A*, 1981, **51**, 55.
9. H. M. IRVING and H S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
10. VAN UITERT and C. HASS, *J. Am. Chem. Soc.*, 1958, **75**, 3651.
11. D. D. PERRIN, "Organic Complexing Agents", Interscience, New York, 1948, p. 51.
12. A. TIWARI, H. N. SHARMA and P. B. CHAKRAWARTI, *Natl. Acad. Sci. Letters*, 1979, **2**, 289.
13. G. HERZBERG, "Molecular Spectra and Molecular Structure, Infra Red and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, 1947.
14. K. FUJITA, K. NAKAMOTO and M. KOBAYASHI, *J. Am. Chem. Soc.*, 1956, **78**, 3963.

Chromatographic Behaviour of Copper(II), Cadmium(II), Bismuth(III), Cobalt(II) and Nickel(II) Ions in Solvents Containing Dimethyl Sulphoxide

K. RAJAMANI, S. MEENAKSHI and W. T. JANAKI*

PSGR Krishnammal College, Coimbatore-641 004

Manuscript received 21 December 1982, revised 26 March 1984, accepted 21 July 1984

THE present investigation is aimed at a study of the effect of dimethylsulphoxide (DMSO) when admixed with solvents of varying polarity on the paper chromatographic migrations of cations, namely Cu^{2+}, Cd^{2+}, Bi^{3+}, Co^{2+} and Ni^{2+}.

Experimental

Solutions of Cu^{II}, Cd^{II}, Bi^{III}, Co^{II} and Ni^{II} ions were prepared from their salts and the mixed solutions were prepared by mixing their individual solutions in suitable proportions.

Pure isopropanol, n-butanol, methylethylketone, chloroform, ethyl acetate, DMSO, and 50% nitric acid were used as eluents. The binary mixtures consisted of different proportions of DMSO in various solvents and adding a definite percentage of 50% nitric acid to minimise the diffusion and increase the sharpness of the band (Table 1).

Rutter's technique[1] of circular paper chromatography was adopted using 12.5 cm circles of Whatman No. 1 chromatographic paper and the elution carried out until the solvent front reached the premarked boundary. 0.05 to 0.1 ml of the solution was spotted containing 10 to 20 μg of the cations. For the comparison of Rr values of the ions Kawerau's modification of Rutter's technique was adopted. The spots were dried at 50-60° in air oven and the ions detected by spraying yellow ammonium sulphide[2].

Results and Discussion

In isopropanol, n-butanol, methylethylketone, the cations show only a diffusive migration. Rr values of the ions increases with increase in polarity. In other nonpolar solvents like ester, chloroform the ions do not migrate at all. However, in DMSO all the ions migrated almost to the solvent front. Due to its highly polar and donor nature, DMSO is capable of desorbing the adsorbed ions and subsequently solubilizes the ions due to its complex forming tendency with ions.

As in the case of pure solvents, the rate of migration of the ions increases with an increase in dielectric constant of the binary system. Thus, with higher concentration of DMSO, the Rr value is at its maximum and migration occurs almost to the solvent front, whereas with low proportion of DMSO the migration of ions was restricted. High donor capacity of DMSO is supported by nonlinear graphs obtained from plot of Rr values of the ions with dielectric constant.

Quantitative separation of binary and ternary ions is possible with solvent systems such as DMSO : isopropanol : HNO_3 (50%) (20 : 70 : 10) ; DMSO : n-butanol : HNO_3 (50%) (10 : 84 : 6), (20 : 74 : 6) ; and DMSO : methylethylketone : HNO_3 (50%) (30 : 60 : 10) (Table 2).

From the above it can be inferred that DMSO plays a dual role in the chromatographic migration of ions on paper in solubilizing the ions, as well as enhancing the rate of migration because of its high polar nature and donor capacity.

TABLE 1—Rf VALUE × 100 OF IONS IN TERNARY SYSTEMS

Solvent system	Cu^{2+}	Ni^{2+}	Co^{2+}	Cd^{2+}	Bi^{3+}
DMSO : n-butanol : HNO_3 (50%)					
10 : 84 : 6	24	18	24	83	63
20 : 74 : 6	47	46	47	50	68
DMSO : Isopropanol : HNO_3 (50%)					
10 : 80 : 10	48	31	39	45	69
20 : 70 : 10	65	62	78	65	91
DMSO : Methylethylketone : HNO_3 (50%)					
10 : 80 : 10	54	39	48	58	85
20 : 70 : 10	62	63	63	69	94
80 : 60 : 10	79	83	72	86	96
DMSO : Ethylacetate : HNO_3 (50%)					
10 : 80 : 10	41	22	23	30	72

TABLE 2—SEPARATION OF BINARY AND TERNARY IONS

Solvent system	Ions separated
DMSO : Isopropanol : HNO_3 (50%) 20 : 70 : 10	Ni^{2+}-Bi^{3+}
	Co^{2+}-Cd^{2+}
	Bi^{3+}-Cd^{2+}
	Bi^{3+}-Cu^{2+}
	Cd^{2+}-Bi^{3+}-Co^{2+}
	Cd^{2+}-Ni^{2+}-Bi^{3+}
DMSO : n-butanol : HNO_3 (50%) 10 : 84 : 6; 20 : 74 : 6	Bi^{3+}-Cd^{2+}-Co^{2+}
	Ni^{2+}-Cd^{2+}-Bi^{3+}
	Co^{2+}-Bi^{3+}
	Co^{2+}-Cu^{2+}(d)
	Ni^{2+}-Cd^{2+}
	Ni^{2+} Cu^{2+}(d)
	Co^{2+}-Cu^{2+}-Bi^{3+}(d)
	Co^{2+}-Bi^{3+}-Cd^{2+}
DMSO : Methylethylketone : HNO_3 (50%) 30 : 60 : 10	Ni^{2+}-Cd^{2+}-Bi^{3+}
	Cu^{2+}-Bi^{3+}-Ni^{2+}
	Co^{2+}-Cd^{2+}-Bi^{3+}

(d) = diffused

References

1. L. RUTTER, *Nature (London)*, 1948, **161**, 435.
2. S. KERTES and M. LEDERER, *Anal. Chim. Acta*, 1956, **15**, 543.

Further Studies in Multiple Boundary Formation During Electrolysis in a W-tube

SUBHALAKSHMI GHOSH

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta-700 032

Manuscript received 28 April 1983, revised 23 March 1984, accepted 21 July 1984

AS early as 1972 Palit[1,2] made the intriguing observation that on electrolysis of any dilute electrolyte in a W-tube, sharp stationary boundaries form in the inner tubes generally dividing the solution into three zones – acid, neutral and alkaline. The intermediate neutral zone is not only neutral but is practically depleted of all electrolytes, a behaviour which is just opposite to the prediction of the time honoured Hittorf theory and so can be termed an anti-Hittorf phenomenon. Time taken for such boundary formation, multiplicity and sharpness of the boundaries, if and whenever formed any, depend on the current density, concentration of the electrolyte[3], cell geometry, nature of the solvent[4] and nature of the electrolyte[4,5]. Sengupta and Palit[6] also noted the acceleration of boundary formation by exogenous addition of acids, alkalis as well as salts into the original electrolytic solution and put forward a tentative theory to explain this phenomenon. During electrolysis of a potassium dichromate solution under various conditions the present author observed some interesting features in addition to those reported earlier[1-6] related to the boundary formation phenomenon, and these are enumerated in the present note.

Band formation in outermost limbs : If initially the lower portion of the W-tube be filled with a mixture of potassium dichromate and a concentrated additional electrolyte (*e.g.* sodium sulphate), the rest with dichromate solution alone, and the system is electrolysed, a colourless band at the anode limb and a deep coloured band at the cathode limb appear. But the development of such a coloured or colourless thin band does not take place, if the entire solution is initially a mixture of potassium dichromate and sodium sulphate.

Double boundary formation in the outermost tube by adding sugar : When the lower part of the W-tube is filled up with a mixture of $K_2Cr_2O_7$ (0.01 *M*) and a concentrated sugar solution, and the rest with original dichromate solution (0.01 *M*), a spectacular boundary formation takes place at the outermost tubes of the W-tube. Initially a colourless band forms in the lower portion of the outermost limb on the cathode side, which gradually spreads out towards the lower portion of the outermost limb on the anode side, current density simultaneously decreasing from 5 to 0.2 mA. The solution above this band assumes light yellow colour on the cathode side and deep brown colour on the anode side. Another important feature of such electrolysis is that no gas formation takes place at all at the intermediate portion of the tube even after prolonged electrolysis.

Effect of adding solid potassium dichromate after double boundary formation with its solution : If about 0.1 g of $K_2Cr_2O_7$ is added from the cathode

side just after the double boundary formation in the electrolysis of (0.005 M) $K_2Cr_2O_7$ solution in a 16 mm o.d. W-tube, the current density gradually increases from a very low value of 0.2 to about 2.5-3 mA and remains steady at that point thereafter. Besides, the alkaline dichromate colour at the cathode side gradually diminishes and becomes completely colourless after about one week. On the otherhand, the colour of the anode limb becomes darker. Therefore, we come across a situation in which the double boundary formation which is very much common with a W-tube, can be converted to a single boundary just by adding excess electrolyte. Similar phenomenon takes place even with the addition of solid $K_2Cr_2O_7$ from both cathode and anode sides at the same time.

Effect of temperature : Temperature has a pronounced effect on the boundary formation in a W-tube. At higher temperature ($\sim 45°$), the electrolysis of 0.005 M $K_2Cr_2O_7$ solution in a W-tube of 16 mm o.d. and at 20 mA current density gives single boundary at the anode bend. After about 48 h current decreases to 10 mA. On cooling down the electrolytic cell to room temperature double boundary forms and the current density decreases to 0.5 mA. At this stage if the temperature is again increased to 45°, the boundary does not diffuse. With wider tube (32 mm o.d.) whose middle part is of the same height as the cathode and the anode limb, electrolysis of 0.01 M chromic acid at 45° in a thermostat and 15 mA current density does not show any boundary formation for overnight and a few cm^3 of gas usually termed as IZ-gas, at the middle portion of the tube is formed. Similar phenomenon is observed with 0.005 M $K_2Cr_2O_7$ solution at 45°. Electrolysis of 0.005 M $K_2Cr_2O_7$ solution in such tube at room temperature takes about 48 h for double boundary formation. Temperature is then increased to 45°, when the boundary diffused and current increased to 12 mA and remained steady thereafter.

Lilliput electrodes—its effect : On electrolysis with lilliput electrodes as cathode and anode, a colourless band first appears at the cathode bend and another boundary appears at the anode bend so that the colour inside the tube from anode to cathode side becomes orange-yellow - colourless band-light yellow. Although, current decreases to 5 mA, the colourless band remains as it is. With the cathode of lilliput size and the foil type anode, the boundary forms quickly. After double boundary formation the colourless band disappears and intermediate zone becomes totally colourless. When the case is reversed by taking lilliput electrode as anode and foil electrode as cathode, little longer time is required for double boundary formation, colourless band remaining at the cathode bend.

Other set-ups equivalent to W-tube : 0.0025 M $K_2Cr_2O_7$ is electrolysed in the set up comprising of two 250 ml beakers connected by an inverted U-tube of 10 mm o.d. platinum foil electrodes are introduced separately into the beakers. Current is passed directly from D.C. mains and within 4 h it becomes 26 mA. No sharp boundary is formed but the solution in the beaker containing the anode becomes darker in colour and that in the other one becomes light yellow. Colour inside the connecting tube becomes deep yellow but on continued electrolysis for overnight, current decreases to 0.8 mA and the middle part becomes colourless. Then another beaker is introduced at the middle to the preceding set-up and connected as before by another inverted U-tube of 10 mm o.d. Here electrolysis of 0.0025 M $K_2Cr_2O_7$ solution for overnight makes only one connecting tube nearer the cathode colourless. The solution in the beaker containing cathode becomes light yellow while two other beakers are orange in colour and the second connecting tube is yellow in colour. This situation remains as it is even on further electrolysis.

Acknowledgement

Thanks are due to late Prof. S. R. Palit for helpful suggestion and discussion.

References

1. S. R. PALIT, *J. Indian Chem. Soc.*, 1972, **49**, 963.
2. S. R. PALIT, *Indian J. Phys.*, 1972, **46**, 430.
3. S. R. PALIT and M. GUHA, *J. Indian Chem. Soc.*, 1974, **51**, 518.
4. S. R PALIT, *J. Indian Chem. Soc.*, 1975, **52**, 114.
5. S. R. PALIT, *J. Soc. Dyers Colour.*, 1975, 846.
6. S. K. SENGUPTA and S. R. PALIT, *J. Indian Chem. Soc.*, 1977, **54**, 724.

Electrochemical Oxidation of Alcohol Held in the Cathode Chamber to Acetic Acid Through Non-Faradaic Electrolysis

SUBHALAKSHMI GHOSH

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta-700 032

Manuscript received 30 November 1983, accepted 21 July 1984

It has been earlier postulated[1] that co-liberation (*i.e.* liberation of a mixture of hydrogen and oxygen) at the cathode during non-Faradaic electrolysis is caused by the formation of $(H_2O)_2^+$ at the anode due to high dielectric constant of water. This H_2O^+ is a free radical ion of oxidative character and so is expected to oxidise substances present in its path of migration to the cathode. Indeed this has been found[2] to be true, even very stable compounds like chlorobenzene, nitrobenzene, *etc* being oxidised when placed in the intermediate zone in the path of the current. If our idea be correct, H_2O^+ formed at the anode would travel towards the cathode and may oxidise substances present at the cathode chamber, though in normal electrolysis the cathode chamber is a seat of reducing activity. Thus under such conditions we may expect to observe the abnormal phenomenon of oxidation in the cathode

chamber. In this note we report such facile oxidation of alcohol held in the cathode chamber presumably caused by the above mechanism.

Experimental

The apparatus was an ordinary U-tube (20 cm × 18 mm o.d.) with a fine fritted glass partition at the bottom (the size not critical). The electrodes were bright platinum foils (1 cm × 1 cm). The cathode side was fitted with a cork through which passed a long vertical tube to take care of the electro-osmotic rise. The catholyte is a 1% solution of ethyl alcohol whereas the anolyte is distilled water. 230 V from D.C. mains are directly applied. Water being highly non-conducting only a few hundred microamperes passed at the beginning. A higher D.C. voltage may be applied if available. The current slowly rose to about 1 mA and somewhat beyond. Due to the high electro-osmotic rise of distilled water at the cathode side, 0.01 N Na_2SO_4 or 0.01 N H_2SO_4 solution was better used instead. About 1-4 mA current was passed for 24 h. Few experiments were also done in a simple U-tube (30 cm × 32 mm o.d.) as used in our previous experiments for the study of non-Faradaic electrolysis[3]. In such U-tube the required amount of alcohol was added very carefully from the cathode side just after the electrolysis started. Electro-osmosis did not take place due to the absence of fritted glass partition at the bottom. Therefore, the experiment was done even with distilled water. But due to very low current density, acid conversion was less than that with 0.01 N or 0.001 N H_2SO_4 solution.

What happens is that H_2O^+ enters the cathode chamber and oxidises the alcohol to acetic acid. The acetic acid as it forms migrates to the anode chamber and so almost the whole product of oxidation formed inside the cathode chamber collects in the anolyte. The amount of acetic acid formed is found by titration with 0.1 N NaOH using phenolphthalein as indicator. Since 4 F are theoretically needed to convert 1 mole alcohol to 1 mole acetic acid ($C_2H_5OH+2O \rightarrow CH_3COOH+H_2O$) and since 1 mA per day is approximately equal to 1 meqv., it is easily seen that if the efficiency is cent per cent, 10 ml 0.1 N alkali would be the titre in 4 days at current strength of 1 mA. The actual efficiency is found to be about 70 to 90 per cent, a remarkable yield.

It may be thought that alcohol is diffusing to the anode chamber and getting oxidised there. The contrary is proved by the fact that in a control experiment no detectable amount of alcohol (acid $K_2Cr_2O_7$ test) is found in the anode chamber consistent with the extremely slow rate of diffusion through such fine 'frit'. Even a N $K_2Cr_2O_7$ solution shows no detectable diffusion in a week. Furthermore, electro-osmotic flow takes place in the reverse direction towards the cathode. A portion (5 to 10%) of acetic acid formed is also found in the cathode chamber itself.

Not only ethyl alcohol, but many other substances are reacted upon in the same way. For example, methyl alcohol is oxidised to formic acid and carbon dioxide, other alcohols to the corresponding acids, urea to ammonia and so on which will be reported in a separate publication. We record here only the remarkable fact that oxidation may take place even in the catholyte with high current efficiency but low power efficiency. Efforts are being made to remove the latter hurdle in order to make the process attractive and cost-efficient.

Acknowledgement

The work has been carried out under the guidance of late Professor S. R. Palit.

References

1. S. R. PALIT and S. GHOSH, *J. Indian Chem. Soc.*, 1979, **56**, 494.
2. S. R. PALIT, *J. Indian Chem. Soc.*, 1973, **50**, 626.
3. S. R. PALIT and S. GHOSH, *J. Indian Chem. Soc.*, 1976, **53**, 1099.

Ultraviolet and Visible Spectral Studies of Anthraquinonyl and Other Hydroxytriazenes

D. N. PUROHIT

Department of Chemistry, S. B. S. H., M. L. Sukhadia University, Udaipur-313 001

Manuscript received 26 December 1983, revised 12 June 1984, accepted 17 June 1984

HYDROXYTRIAZENES, also called diazohydroxyamino compounds and triazen oxides[1] have been established as an important group of chelating agents[2,3]. There is a growing interest[4-7] in these compounds. In this communication the ultraviolet and visible spectral studies of nine hydroxytriazenes have been reported.

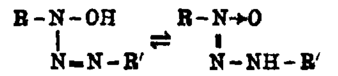
Experimental

The ultraviolet and visible absorption spectra were taken in absolute alcohol on a Beckmann DB spectrophotometer using quartz and glass cells of 1.0 cm pathlength. The results obtained (λ_{max}, logϵ) are given in Table 1.

From Table 1 it is not possible to make any exact correletion with the structure. Still the following points are noteworthy.

(a) Compounds no. 1, 2 and 3 show two absorption maxima. The first one appears at 418-420 nm which may be assigned to n-π^* transition. The second one appears in the range 300-388 nm and specifically at 347 ± 5 nm in compounds no. 1, 2 and 3. It seems to be due to the conjugation between $-N=N-$ and the aryl nucleus and may be designated as π-π^* transition.

TABLE 1



I II

Sl. no.	Hydroxytriazenes (I) R	R′	λ_{max} EtOH (nm)	Triazen oxide (II) log ε
1.	CH_3	2′-anthraquinonyl	842	4.818
			420	4.029
2.	C_2H_5	2′-anthraquinonyl	842	4.107
			418	3.798
3.	C_6H_5	2′-anthraquinonyl	852	4.488
			420	4.207
4.	C_6H_5	o-carboxyphenyl	218	4.401
			242	4.965
			868	4.531
5.	CH_3	o-nitrophenyl	204-210	?.886
			256-264	4.200
			284-292	4.200
			888	3.755
6.	CH_3	p-nitrophenyl	214	3.961
			242	3.209
			276	3.079
			364	3.792
7.	n-C_3H_7	phenyl	222-223	3.997
			291	4.162
			310-312	4.189
8.	n-C_3H_7	p-tolyl	222	4.189
			292	4.162
			310-312	3.977
9.	*N*-1,1′-(2,2′-Dimethyl-4,4′-biphenyleno)-bis(3-*N*-hydroxy-3-ethyltriazene)		218	4.401
			242	4.865
			368	4.531

(b) In compounds no. 5 to 8 an absorption maximum appears in the range 276-292 nm, which may be taken to indicate that there is a greater contribution of the triazene oxide form (II) in these compounds. Disappearance of this band in compounds no. 1 to 4 and 9 is difficult to explain but it seems that a lesser contribution of the hydroxytriazene form (I) may be responsible for this phenomenon.

(c) In compounds no. 4 to 9 there appears a band in the range 214 to 228 nm and an additional band at 253±11 nm in compounds no. 4, 5, 6 and 9, which may be correleted to the π-π^* band of benzene displaced to the longer wavelengths due to substitution on the benzene ring.

References

1. E. H. RODD, (Ed.), "Chemistry of Carbon Compounds", Vol. IIIA, p. 807.
2. D. N. PUROHIT, *Talanta*, 1967, **14**, 353.
3. D. CHAKRABORTI and A. K. MAJUMDAR, *J. Indian Chem. Soc.*, 1977, **54**, 258.
4. P. D. CHATLANGYA, C. S. BHANDARI and N. C. SOGANI, *J. Indian Chem. Soc.*, 1977, **54**, 1001.
5. N. R. BISWAS, B. C. ROY and S. LAHIRI, *J. Indian Chem. Soc.*, 1979, **56**, 478 ; 1981, **58**, 807, 1138.
6. R. L. DUTTA and R. SHARMA, *J. Indian Chem Soc.*, 1980, **57**, 559 ; 1981, **58**, 807 ; *J. Inorg. Nucl. Chem.*, 1981, **43**, 1062.
7. K. MUKKANTI, Y. K. BHOON, K. B. PANDEYA and R. P. SINGH, *J. Indian Chem. Soc.*, 1982, **59**, 830.

Preparation and Antibacterial Activities of 2-Aryl-3-[α-(2-hydroxy-1-naphthyl)benzyl]-4-thiazolidinones

N. C. DESAI, H. K. SHUKLA, N. A. LANGALIA

and

K. A. THAKER

University Department of Chemistry, Bhavnagar University, Bhavnagar-364 002

Manuscript received 4 June 1982, revised 30 March 1984, accepted 30 May 1984

THIAZOLIDINONES, the derivatives of thiazolidine having a carbonyl group at 2, 4 or 5 position, have been studied in detail recently[1-8]. Several reviews have been written on thiazolidinones which highlight their chemistry and implications[9-13]. The present investigation has been undertaken to compare the effect of azomethines (II) and thiazolidinones (III) on antimycobacterial and antibacterial activity. The 2-aryl-3-[α-(2-hydroxy-1-naphthyl)-benzyl]-4-thiazolidinones (III) have been prepared by the reaction of mercaptoacetic acid with azomethines (II) and tested against *Mycobacterium tuberculosis* ($H_{37}Rv$), *E.coli* and *S. aureus*.

The structure of the title compound (III) has been elucidated on the basis of their elemental analysis, ir and uv spectra. The Schiff bases (II) gave strong band in the region 1630-1615 cm^{-1}, which disappeared by thiazolidine ring formation. The compound III showed λ_{max} at 235, 342 nm and ν_{max} at 1630 and 1655 cm^{-1}. The ir spectra were recorded on Backman IR 20 spectrophotometer.

Experimental

α-(2-Hydroxy-1-naphthyl)-benzylamine (I) has been prepared following the method described in the literature[14,15].

Azomethines (II) : The appropriate aldehyde (0.01 mol) and I (0.01 mol) were dissolved in EtOH (95%, 50 ml) and the solution refluxed for 3 h, the excess solvent distilled until the Schiff base commenced to crystallise (Table 1 and 3).

4-Thiazolidinones (III) : The mixture of appropriate azomethine (II, 0.01 mol) and thioglycolic acid (0.01 mol) in anhydrous benzene (30 ml) was refluxed for 8 h and the excess solvent and thioglycollic acid removed under vacuum. The residue was washed thoroughly with aqueous $NaHCO_3$ and water, dried and crystallised from ethanol (95%) (Table 2 and 3).

Pharmacological screening : The *in vitro* antitubercular activity of the compounds I, II and III was studied against $H_{37}Rv$ strain of *Mycobacterium tuberculosis* in Lowenstein-Jensen egg media at 0.02 mg/ml. The retardafion of the growth rate has been studied upto 6 weeks at 37°.

The antibacterial activities of the compounds I, II and III were tested by N-agar pour-plate

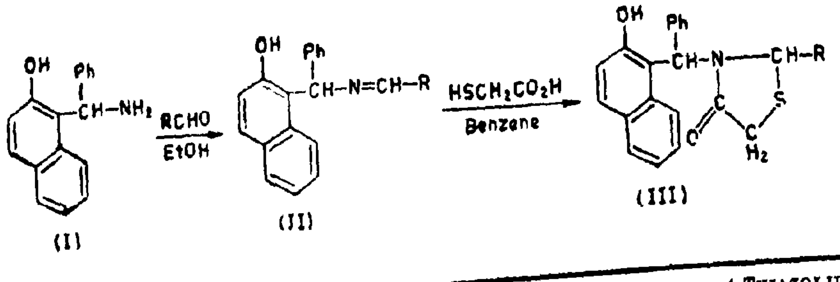


TABLE 1—PHYSICAL DATA OF AZOMETHINES (II)

Sl. no.	R	M.p. °C	(Analysis % N : Found/Calcd.)
1.	C_6H_5	146	4.19 (4.00)
2.	2.OH.C_6H_4	176	4.22 (3.96)
3.	4.OH.C_6H_4	152	4.21 (3.96)
4.	4.Cl.C_6H_4	162	4.02 (3.76)
5.	4.OCH$_3$.C_6H_4	95	3.52 (3.81)
6.	5.Br.2-OH.C_6H_3	109	3.56 (3.24)
7.	3,5-di-Br.2-OH.C_6H_2	80	3.04 (2.73)
8.	3,4-CH$_2$.O$_2$.C_6H_3	145	3.96 (3.67)
9.	4.NO$_2$.C_6H_4	90	6.92 (7.32)
10.	3.NO$_2$.C_6H_4	170	6.98 (7.32)
11.	4.CH$_3$.C_6H_4	169	4.21 (3.98)

method in DMF and found to be active against *E.coli* and *S.aureus*.

On comparison of the experimental data, it has been observed that the compounds I and II do not possess significant antimycobacterial activity and the presence of thiazolidine nucleus is necessary for potential antitubercular activity, and the presence of the halogen atoms in II and III enhances the antibacterial activity.

TABLE 2—PHYSICAL DATA OF 4-THIAZOLIDINONES (III)

Sl. No.	R	M.p. °C	Analysis % : Found/(Calcd.) N	S
1.	C_6H_5	132	3.76 (3.40)	7.99 (7.78)
2.	2-OH.C_6H_4	154	3.61 (3.27)	7.95 (7.49)
3.	4.OH.C_6H_4	138	3.89 (3.27)	7.98 (7.49)
4.	4.Cl.C_6H_4	154	2.98 (3.14)	7.91 (7.18)
5.	4.OCH$_3$.C_6H_4	127	3.49 (3.17)	6.91 (7.25)
6.	5-Br.2-OH.C_6H_3	119	2.98 (2.76)	6.59 (6.32)
7.	3,5-di-Br-2-OH.C_6H_2	112	2.78 (2.39)	4.98 (5.47)
8.	3,4-CH$_2$.O$_2$.C_6H_3	179	3.32 (3.07)	7.22 (7.03)
9.	4-NO$_2$.C_6H_4	132	5.98 (6.14)	7.20 (7.01)
10.	3.NO$_2$.C_6H_4	200	6.01 (6.14)	7.42 (7.01)
11.	4.CH$_3$.C_6H_4	191	3.49 (3.29)	7.72 (7.52)

TABLE 3—ANTIBACTERIAL AND ANTITUBERCULAR ACTIVITY OF COMPOUNDS II AND III

Sl. no.	R	Antibacterial activity of II: Interpretation zone of inhibition at 100 µg concn./disk		Antitubercular and antibacterial activity of III: Interpretation zone of inhibition at 100 µg concn./disk		Antituberculosis activity $H_{37}R_v$
		S. aureus	*E. coli*	*S. aureus*	*E. coli*	
1.	C_6H_5	−	−	−	−	+
2.	2.OH.C_6H_4	−	−	+	−	+
3.	4.OH.C_6H_4	+	−	−	−	+
4.	4.Cl C_6H_4	++	−	+	−	+
5.	4.OCH$_3$.C_6H_4	+	+	+	+	+
6.	5.Br.2-OH.C_6H_3	+	−	+	+	+
7.	3,5-di-Br.2.OH.C_6H_2	++	+	++	+	+
8.	3,4-CH$_2$.O$_2$.C_6H_3	+	−	−	−	+
9.	4.NO$_2$.C_6H_4	−	−	+	−	+
10.	4.NO$_2$.C_6H_4	−	−	−	−	+
11.	4.CH$_3$.C_6H_4	−	−	+	−	+

(−) = Zone diameter of growth inhibition in mm.
(+) = Zone diameter less than 20 mm.
(++) = Zone diameter more than 20 mm.
The tuberculostatic concentration, 0.02 mg/ml.

Acknowledgement

The authors are thankful to Bhavnagar University for providing research fellowships (N.C.D. and H.K.S.) and also to Dr. S. B. Trivedi, Director, Tuberculosis Research Centre, Amargadh, for screening the samples.

References

1. A. R. Surrey, *J. Am. Chem. Soc.*, 1949, **71**, 3354.
2. H. D. Trautman and L. M. Long, *J. Am. Chem. Soc.*, 1948, **70**, 3436.
3. H. K. Shukla, R. R. Astik and K. A. Thaker, *J. Indian Chem. Soc.*, 1981, **58**, 1182.
4. A. J. Cowper, R. R. Astik and K. A. Thaker, *J. Inst. Chem., Calcutta*, 1981, **53**, 111.
5. S. Nagar, H. H. Singh, J. N. Sinha and S. S. Parmar, *J. Med. Chem.*, 1973, **16**, 178.
6. H. C. Tong and D. Skidmove, *Chem. Abstr.*, 1975, **83**, 109744.
7. G. R. Hendricks, *J. Med. Pharm. Chem.*, 1965, **8**, 762.
8. H. D. Treutman and L. M. Long, *J. Am. Chem. Soc.*, 1951, **66**, 829.
9. F. C. Brown, *Chem. Rev.*, 1961, **61**, 463.
10. K. A. Zolotoreva, I. P. Maslova, N. A. Glazunova, E. F. Burmistrov and L. A. Pugacheva, *Chem. Abstr.*, 1966, **65**, 18767.
11. G. Danila, *Rev. Chim. (Bucharest)*, 1978, 29, 820 (*Chem. Abstr.*, 1979, **90**, 72086).
12. G. Danila, *Rev. Chim. (Bucharest)*, 1978, **29**, 1152 (*Chem. Abstr.*, 1979, **90**, 152087).
13. S. P. Singh, S. S. Parmar, Krishan Raman, V. I. Stenberg, *Chem. Rev.*, 1981, **81**, 175.
14. A. H. Blatt, *Org. Synth.*, 1967, **1**, 381.
15. M. Betti, *Gazz. Chim. Ital.*, 1901, **1**, 381.

Synthesis of 5-Mercapto-4-Amino-3-Substituted-1,2,4-Triazoles and Their Mono- and Disulphide Derivatives

S. A. PATIL, B. M. BADIGER, S. M. KUDARI
and
V. H. KULKARNI*

Department of Chemistry, Gulbarga University, Gulbarga-585 106

Manuscript received 28 June 1982, revised 26 March 1984, accepted 17 June 1984

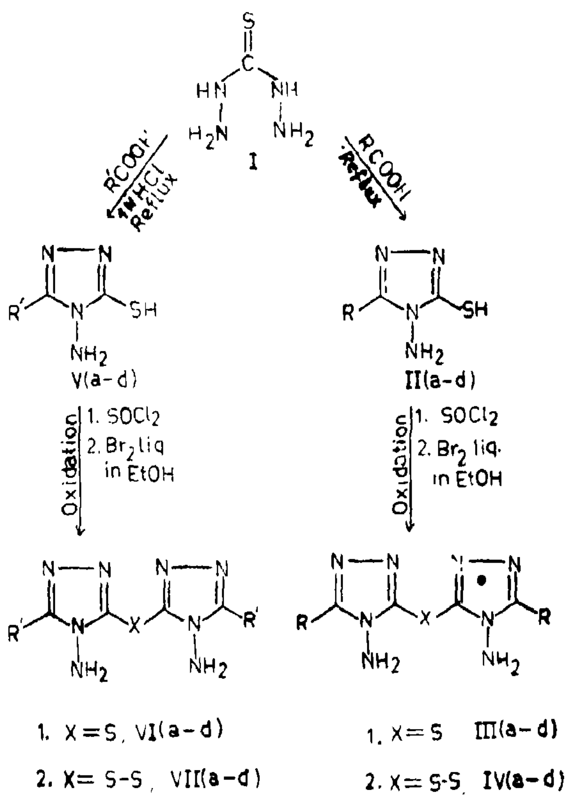
TRIAZOLES and their derivatives have been proved to be effective bactericides[1], pesticides[2] and fungicides[3,4]. They have been used in the gravimetric estimations of silver, copper and lead[5-8]. In this communication we report a few new derivatives of triazoles.

The compounds **IIa-d** (Table 1) are prepared according to the known method[9]. They are characterised by elemental analysis and ir spectra. These compounds on oxidation with thionylchloride and bromine in absolute ethanol, respectively yield monosulfides (**IIIa-d**) and disulphides (**IVa-d**). The compounds **Va-f** are prepared in 4*N* HCl and oxidised to their respective sulphides (**VIa-d**) and disulphides (**VIIa-d**)[2].

Table 1—3-Substituted-4-amino-5-mercapto-1,2,4-triazoles (IIa-d and Va-f)

Compd. no.	R/R'	M.p. °C	Analysis % ; Found/(Calcd.) C	H	N	S
IIa	H	108	20.15 (20.69)	3.51 (3.45)	48.00 (48.28)	27.72 (27.59)
IIb	CH_3	218-19	26.23 (27.69)	4.65 (4.62)	42.81 (43.08)	24.47 (24.62)
IIc	C_2H_5	140-41	33.00 (33.33)	5.64 (5.56)	38.79 (38.89)	22.30 (22.22)
IId	C_3H_7	72-74	38.45 (37.97)	4.95 (6.33)	48.01 (35.44)	21.87 (20.25)
Va	C_6H_5	234	48.57 (50.00)	4.02 (4.17)	28.78 (29.17)	16.52 (16.66)
Vb	o-OH-C_6H_4	228-30	46.18 (46.15)	3.60 (3.85)	26.59 (26.92)	15.45 (15.38)
Vc	o-H_2N-C_6H_4	242	46.35 (46.38)	4.75 (4.83)	33.70 (33.82)	15.08 (15.46)
Vd	p-H_2N-C_6H_4	230	46.30 (46.38)	4.80 (4.83)	33.61 (33.82)	15.45 (15.46)
Ve	CH_2CN	241-42	30.55 (30.96)	3.19 (3.23)	45.00 (45.16)	20.41 (20.65)
Vf	CH_2NH_2	250-51	24.80 (24.82)	4.78 (4.83)	48.25 (48.27)	22.00 (22.07)

The synthetic route for these compounds is shown below.



Infrared spectra : All the triazoles exhibit a medium to high intensity band in the 1660-1610 cm^{-1} region attributable to $\nu_{C=N}$. The band due to ν_{NH} associated with the thione form appears in the 3330-3225 and 3200-3150 cm^{-1} regions. The ν_{SH} appears in the region 2600-2500 cm^{-1}. For compounds **Ve** $\nu_{C\equiv N}$ appears at 2200 cm^{-1}.

TABLE 2—BIS(4-AMINO-3-SUBSTITUTED-1,2,4-TRIAZOLE-5-YL)MONO (IIIa-d AND VIa-d) AND DI (IVa-d AND VIIa-d) SULPHIDES

Compd. no.	R'	X	M.p. °C	Analysis % ; Found/(Calcd.) C	H	N	S
IIIa	H	S	110-12	23.78 (24.24)	3.00 (3.03)	56.05 (56.57)	15.98 (16.16)
IIIb	CH_3	S	251	31.00 (31.86)	4.31 (4.42)	49.50 (49.56)	14.01 (14.16)
IIIc	C_2H_5	S	255-56	37.25 (37.80)	5.37 (5.51)	44.13 (44.09)	12.61 (12.51)
IIId	C_3H_7	S	191-92	43.00 (42.55)	6.41 (6.38)	39.68 (39.72)	10.85 (11.35)
VIa	C_6H_5	S	78	55.70 (54.86)	4.08 (4.00)	32.00 (32.00)	9.21 (9.14)
VIb	o-HO-C_6H_4	S	253-55	50.00 (50.26)	3.78 (3.66)	29.48 (29.32)	8.51 (8.38)
VIc	o-H_2N-C_6H_4	S	250	50.12 (50.53)	4.16 (4.21)	36.80 (36.84)	8.33 (8.42)
VId	p-H_2N-C_6H_4	S	116-18	50.53 (50.58)	4.11 (4.21)	36.96 (36.84)	8.34 (8.42)
IVa	H	S-S	135-38	20.57 (20.87)	2.59 (2.61)	48.50 (48.70)	27.77 (27.83)
IVb	CH_3	S-S	155	27.02 (27.91)	3.90 (3.88)	42.78 (43.41)	23.95 (24.81)
IVc	C_2H_5	S-S	185	33.56 (33.57)	4.81 (4.90)	39.00 (39.16)	22.71 (22.38)
IVd	C_3H_7	S-S	115-16	38.51 (38.22)	5.74 (5.73)	35.23 (35.67)	20.00 (20.38)
VIIa	C_6H_5	S-S	85	49.76 (50.26)	3.60 (3.66)	29.00 (29.32)	16.89 (16.75)
VIIb	o-HO-C_6H_4	S-S	196-98	46.80 (46.38)	3.74 (3.38)	28.75 (27.05)	15.35 (15.46)
VIIc	o-H_2N-C_6H_4	S-S	198-200	46.50 (46.60)	3.72 (3.88)	33.03 (33.98)	15.50 (15.53)
VIId	p-H_2N-C_6H_4	S-S	145-46	46.14 (46.60)	3.78 (3.88)	32.89 (33.98)	15.36 (15.53)

Biological activity : All the reported compounds have been evaluated for their antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli*. Almost all the mercaptotriazoles (**IIa-d** ; **Va-f**) are found to be more active against *S. aureus* than their mono- and disulphide. The compound **Vf** has shown better activity (15 mm) than the others. **VIa** has exhibited the highest inhibition (18 mm) against gram -ve organism *E. coli*. The others which have shown moderate activity against *E. coli* are **IIIb-d**, **IVc** and **IVd**.

Experimental

The m.ps. are uncorrected. The *ir* spectra (nujol) were recorded on a Perkin Elmer-297 spectrophotometer.

Thiocarbohydrazide (**I**) was prepared by the known method[10]. The compounds **IIa-d** were prepared according to the method reported[9].

Acknowledgement

Authors thank Prof. S. P. Hiremath, Head, Department of Chemistry for his interest and encouragement. One of the authors (S.A.P.) is grateful to C.S.I.R., New Delhi for the financial assistance. Thanks are also due to Mr. and Mrs. P. M. Nimbargi of Microbiology Department, Gulbarga University, for microbial screening.

References

1. A. K. SENGUPTA, O. P. BAJAJ and U. CHANDRA, *J. Indian Chem. Soc.*, 1978, **55**, 962.
2. H. SINGH, L. D. S. YADAV and B. K. BHATTACHARYA, *J. Indian Chem. Soc.*, 1979, **56**, 1013 ; and references therein.
3. S. GIRI, H. SINGH, L. D. S. YADAV and R. K. KHARE, *J. Indian Chem. Soc.*, 1978, **55**, 168.
4. S. RAO and A. S. MITTRA, *Indian J. Chem.*, *Sect. B*, 1977, **15**, 1062.
5. R. V. GADAG and M. R. GAJENDRAGAD, *Talanta*, 1978, **25**, 418.
6. R. V. GADAG and M. R. GAJENDRAGAD, *Indian J. Chem.*, *Sect. A*, 1978, **16**, 703.
7. R. V. GADAG and M. R. GAJENDRAGAD, *J. Indian Chem. Soc.*, 1978, **55**, 789.
8. B. SINGH, R. SINGH, K. P. THAKAR and M. CHANDRA, *Indian J. Chem.*, 1974, **12**, 631.
9. K. S. DHAKA, J. MOHAN, V. K. CHANDA and H. K. PUJARI, *Indian J. Chem.*, 1974, **12**, 288.
10. L. F. AUDRIETH, E. S. SCOTT and P. S. KIPPER, *J. Org. Chem.*, 1954, **19**, 733.

Synthesis and Antifungal Activity of 3-Furyl and 3-Thienyl-substituted-1,2-benzisoxazoles

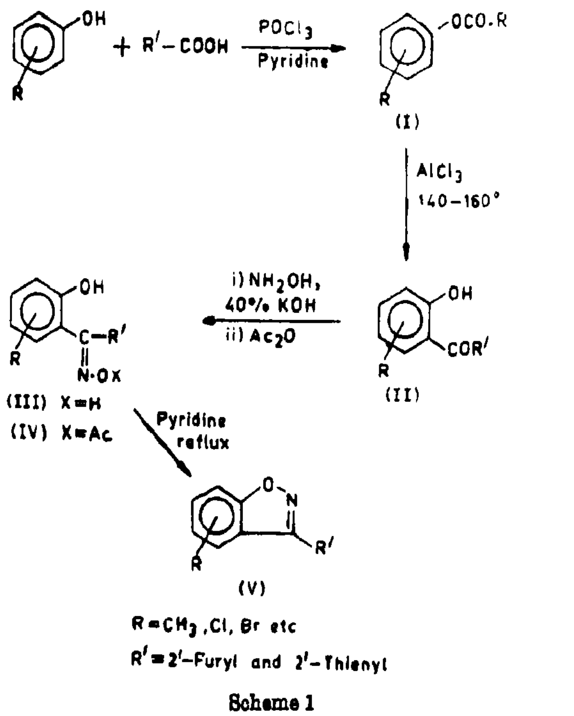
K. A. THAKAR and A. M. PADHYE*

Department of Chemistry, Marathwada University, Aurangabad-431 001

Manuscript received 30 September 1982, revised 10 March 1984, accepted 17 June 1984

HETEROCYCLIC nuclei play a prominent role in bestowing activity on organic compounds. A survey of the literature revealed that very few benzisoxazoles with heterocycles like furan and thiophene are known[1] because of the difficulty in the synthesis of the starting material. 1,2-Benzisoxazoles exhibit a wide variety of activity like antidepressant[2], antibacterial[3], tuberculostatic[4], antifungal[5] *etc.* Since an introduction of a heteryl nucleus is likely to modify the activity of benzisoxazoles, a few 3-heteryl-1,2-benzisoxazoles were synthesised.

Various substituted phenols were esterified (I) with 2-furoic and 2-thiophenic acids by the reported procedure[6]. *Ortho*-hydroxy-phenyl-heteryl-ketones (II) were obtained after Fries' migration of these esters. Oximes (III) and *N*-acetates (IV) of the above ketones were prepared[7] and the corresponding benzisoxazoles (V) were obtained[8] through *N*-acetates (Scheme 1).



Scheme 1

Experimental

All m.ps. were taken in an open capillary and are uncorrected. Ir (nujol, ν, cm^{-1}) were recorded on Beckman 120 and 137 spectrophotometer and nmr spectra ($CDCl_3$) on a Varian 100 MHz spectrophotometer using TMS as an internal standard. Chemical shifts are expressed in δ, ppm.

Esterification of phenols with 2-furoic and 2-thiophenic acids was carried out by following the reported procedure[6].

2-Hydroxy-4,5-dimethyl-phenyl-furyl-ketone : A mixture of heteroyl ester (0.1 mol) and powdered anhydrous $AlCl_3$ (0.2 mol) was heated in an oil bath at 140-150° for 3-4 h. The complex was decomposed with ice-water containing HCl. The *ortho*-isomer was separated from *para*-isomer by steam distillation and crystallised from ethanol to yield the product (56%), m.p. 114°, ν_{max} 1600 (C=O), 760-720 cm^{-1} (furyl), no hydroxy frequency because of chelation ; δ 2.16 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), furyl group protons 6.56 (dd, J 2 Hz, 1H, ArC'$_4$H), 7.26 (dd, J 2 Hz, 1H, ArC'$_3$H), phenyl group protons, 6.74 (s, 1H, ArC$_3$H), 7.9 (s, 1H, ArC$_6$H), 12.5 (s, 1H, OH).

Rest of the ketones were prepared in the similar manner. Physical data of all these compounds are listed in Table 1.

Ortho-hydroxy-phenyl-ketoximes and *ortho*-hydroxy-phenyl-ketoxime-*N*-acetates were prepared by following the reported procedure[7]. Physical data of all these compounds are also listed in Table 1.

3-(2'-Furyl)-5-methyl-1,2-benzisoxazole : Oxime acetate (1 g) and dry pyridine (15 ml) were refluxed for 6 h. Excess of pyridine was then distilled off and the reaction mixture poured on ice-water containing HCl. The product obtained was extracted with ether and washed with dilute aqueous NaOH. Ethereal layer was evaporated to get a solid which on crystallisation from ethanol (40%) yielded the product (66%), m.p. 60° ; ν_{max} 840 (isoxazole-ring-stretch), 1220 (C–O–N) and 1550 (C=N stretching) and 760-930 cm (furyl) ; δ 2.25 (s, 3H, CH_3), 6.44 (dd, J 2 Hz, 1H, ArC$_4$'H), 7.02 (dd, J 2 Hz, 1H, ArC$_3$'H), 7.2 (dd, J 2 Hz, 1H, ArC$_5$'H) of furyl ring ; 7.24 (d, J 2 Hz, ArC$_4$H), 7.56 (dd, J 2 and 8 Hz, 1H, ArC$_6$H), 7.6 (d, J 8 Hz, 1H, ArC$_7$H) of phenyl ring.

All the other cyclised compounds were prepared by following similar procedure and their physical data are listed in Table 2.

Antifungal activity : Fourteen of the compounds (V) listed in Table 2 were tested for antifungal activity by the paper disc method[9] against *Helminthosporium appaternae*, a wheat pathogen and compound of Sl. no. 14 showed maximum and promising activity (inhibited 57 mm of fungus growth) followed by compounds of Sl. no. 13, 15 and 18. Compounds of Sl. no. 2, 4, 5, 7, 8, 10, 19, 20 showed considerable activity, while 6 and 17 were found to be inactive.

* Organic Chemistry Division, National Chemical Laboratory, Poona-411 008.

TABLE 1—PHYSICAL DATA OF COMPOUNDS I-IV

Sl. no.	R′	R	Compd. I		Compd. II		Compd. III		Compd. IV	
			M.p. °C	Yield %	M.p. °C	Yield %	M.p. °C	Yield %	M.p. °C	Yield %
1.	2′-furyl	H	50[a]	60	—	60*	134[b]	50	126[b]	90
2.	,,	2-Cl	65[a]	90	65[b]	50	169[f]	40	102[b]	70
3.	,,	3-OH,	43[a]	70	vis-liq.	85*	126[d]	25	125[d]	40
4.	,,	4-Cl	87[b]	90	93[b]	70*	159[d]	53	110[d]	50
5.	,,	4-OH,	65[b]	70	73[b]	65*	120[g]	80	130[b]	68
6.	,,	2,4-diCl	85[a]	90	115[b]	70*	170[b]	45	134[f]	50
7.	,,	3,4-diOH,	58[b]	77	114[b]	56*	100[d]	80	126[b]	40
8.	,,	4-Br	98[a]	86	90[d]	70*	160[b]	65	140[b]	60
9.	,,	2,4-diBr	96[a]	73	105[b]	80	170[b]	40	120[b]	44
10.	,,	2-OH,,4-Cl	85[a]	90	140[b]	60	145[b]	56	155[b]	64
11.	,,	3-OH,,4-Cl	69[c]	92	100[b]	83	145[b]	68	124[b]	97
12.	2′-thienyl	H	59[a]	50	vis-liq.	30	147[b]	50	110[e]	75
13.	,,	4-Cl	87[b]	75	80[b]	66	125[b]	58	142[b]	74
14.	,,	4-OH,	92[c]	90	125[e]	82	119[g]	66	125[e]	68
15.	,,	3-OH,	86[a]	70	84[e]	48	160[b]	50	107[e]	60
16.	,,	3,4-diOH,	62[a]	50	95[e]	66	117[d]	50	108[b]	72
17.	,,	2,4-diCl	80[a]	55	98[c]	73	169[h]	63	130[b]	60
18.	,,	2,4-diOH,	61[a]	65	84[h]	66	146[g]	60	136[b]	90
19.	,,	2-OH,,4-Cl	88[a]	72	56[b]	66	160[d]	60	121[e]	50
20.	,,	4-Br	84[a]	66	58[b]	66	100[e]	64	140[b]	72

Compd. crystallised from : a = Petroleum ether, b = Aq. EtOH, c = MeOH, d = Aq. AcOH, e = Aq. MeOH, f = Benzene, g = Ligroin, h = Toluene + petroleum ether.
*Reported in the literature.
All the compounds gave satisfactory C, H analyses.

TABLE 2—PHYSICAL DATA AND ANTIFUNGAL ACTIVITY OF COMPOUNDS V

R′ = 2′-furyl (compds. Sl. no. 1-11),
2′-thienyl (compds. Sl. no. 12-20)

Sl. no.	R	M.p. °C	Yield %	Activity against *H. appaternae* Zone of inhibition mm
1.	H	(Thick liquid)	23	–
2.	7-Cl	107[a]	20	13
3.	6-OH,	96[a]	40	–
4	5-Cl	104[a]	29	9
5.	5-OH,	60[a]	66	26
6.	5,7-diCl	150[a]	29	0
7.	5,6-diOH,	115[a]	32	18
8.	5-Br	117[b]	24	12
9.	5,7-diBr	149[c]	11	–
10.	5-Cl, 7-OH,	109[a]	33	11
11.	5-Cl, 6-OH,	135[a]	33	–
12.	H	75[a]	20	–
13.	5-Cl	104[d]	25	48
14.	5-OH,	50[e]	20	57
15.	6-OH,	–	20	–
16.	5,6-diOH,	104[f]	20	39
17.	5,7-diCl	105[a]	20	0
18.	5,7-diOH,	108[a]	20	31
19.	5-Cl, 7-OH,	100[a]	45	16
20.	5-Br	89[e]	15	20

Compds. crystallised from : a = Aq. EtOH, b = MeOH + AcOH, c = EtOH + AcOH, d = MeOH, e = petroleum ether, f = benzene + petroleum ether.

Acknowledgement

One of the authors (A.M.P.) is thankful to Marathwada University for the award of Junior Research Fellowship. Thanks are also due to (Miss) I. Pappu for screening the antifungal activity.

References

1. T. SASKAI and T. YOSHIOKA, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 826.
2. H. NISHIMURA, M. SHIMIZU, H. UNO, T. HIROOKA, Y. MASUDA and M. KUROKAWA, *Jap. Pat.* 74116056, 74116057 (*Chem. Abstr.*, 1975, **83**, 10088, 10089).
3. B. M. BHAWAL, G. V. UMALKAR, D. S. MUKADAM and K. A. THAKAR, *Marathwada University J. Sci., Nat. Sci.*, 1977, **16**, 7 (*Chem. Abstr.*, 1979, **89**, 100772).
4. A. J. C. VAN DER STELT, A. J. ZWART VOORSPUIJ and W. THN. NAUTA, *Arzneim.-Forsch.*, 1954, **4**, 544 (*Chem. Abstr.*, 1955, **49**, 10887).
5. G. V. UMALKAR, B. M. BHAWAL, S. S. BEGUM and K. A. THAKAR, *Indian J. Exptl. Biol.*, 1977, **15**, 406.
6. P. N. WADODKAR and M. G. MARATHEY, *Indian J. Chem.*, 1972, **10**, 145.
7. A. H. BLATT and L. A. RUSSEL, *J. Am. Chem. Soc.*, 1936, **58**, 1903.
8. K. A. THAKAR, D. D. GOSWAMI and B. M. BHAWAL, *Indian J. Chem., Sect. B*, 1977, **15**, 1058.
9. H. H. THORNBERRY, *Phytopathology*, 1950, **40**, 419.

Synthesis of Possible Antiprotozoal Agents

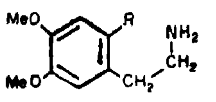
B. R. SARKAR, D. GHOSH and B. C. PATHAK

Department of Chemical Technology, University College of Science, 92, Acharya P. C. Road, Calcutta-700 009

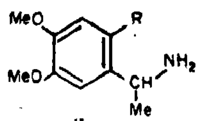
Manuscript received 8 December 1982, revised 30 November 1983, accepted 26 May 1984

BASED on the amebicidal property of emetine several hypothetically modified structural products were synthesised and tested for their antiamebic activity[1-6]. A number of compounds of the types I and II were prepared[7] and in both these types, the compounds (R = n-hexyl) were appreciably active *in vitro* against *E. histolytica*[8]. A number of

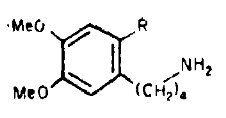
4-(2-alkyl-4,5-dimethoxyphenyl)-n-butylamines (III) were prepared[9] to investigate their amebicidal properties and they showed high *in vitro* amebicidal activity[10] against *E. histolytica*. The object of the present work is to observe whether amebicidal activity is retained in a molecule of the type IV.



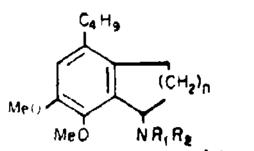
I



II



III



n = 3, 4 ; R1 = R2 = H, alkyl

IV

3,4-Dimethoxy-n-butylbenzene on reaction with succinic or glutaric anhydride produced 3-(2-n-butyl-4,5-dimethoxybenzoyl)-propionic acid or 4-(2-n-butyl-4,5-dimethoxybenzoyl)-butyric acid. The keto acids on Clemmensen reduction yielded 4-(2-n-butyl-4,5-dimethoxyphenyl)-butyric acid and 5-(2-n-butyl-4,5-dimethoxyphenyl)-valeric acid. Cyclisation of the acids in PPA gave ketones. The ketoximes on reduction gave amines and the latter were converted to various secondary and tertiary amines.

Experimental

All melting points and boiling points are uncorrected. Ir spectra were taken in Perkin-Elmer model 237B spectrophotometer. Pmr spectra ($CDCl_3$) were recorded at 90 MHz with TMS as an internal reference on a Varian EM-390 spectrometer. Mass spectra were recorded on an AEI MS-3074 instrument. Elemental analytical data of the compounds tallied with the calculated values based on the molecular formulae of the compounds.

4-(2-n-Butyl-4,5-dimethoxybenzoyl)-butyric acid : Anhydrous aluminium chloride (48 g, 0.36 mol) was slowly added to a chilled (0-5°) stirred mixture of 3,4-dimethoxy-n-butylbenzene (32.98 g, 0.17 mol), glutaric anhydride (20.0 g, 0.18 mol) in dry tetrachloroethane (200 ml) and dry nitrobenzene (50 ml). After standing for three days the usual isolation procedure was followed. The crude keto acid after methylation with Me_2SO_4 (25 ml) in presence of dil sodium hydroxide (10%) was crystallised from petroleum ether (b.p. 60-80°) (24.2 g, 46.2%), m.p. 88-90° ; ν_{max} (KBr) 1675, 1725 cm^{-1}.

5-(2-n-Butyl-4,5-dimethoxyphenyl)-valeric acid : It was obtained by Clemmensen reduction of 4-(2-n-butyl-4,5-dimethoxybenzoyl)-butyric acid. It distilled at 210-215°/2 mm (72.07%) ; ν_{max} (Film) 1700 cm^{-1} (CO).

5-n-Butyl-7,8-dimethoxy-1,2,3,4-tetrahydro-1-keto-naphthalene : A mixture of 4-(2-n-butyl-4,5-dimethoxyphenyl)-n-butyric acid[13] (20 g) and polyphosphoric acid (200 g) was heated under stirring in anhydrous condition on a waterbath at 75° for 40 min. The reaction mixture was poured into a mixture of ice and water, and the organic materials was extracted with benzene. It boiled at 185-6°/1.5 mm (10 g, 53%) ; ν_{max} (Film) 1675 cm^{-1} (CO).

1-n-Butyl-3,4-dimethoxy-6,7,8,9-tetrahydro-5-H-benzocyclohepten-5-one : It boiled at 172-74°/1 mm (64%) ; ν_{max} (Film) 1690 cm^{-1} (CO) ; δ($CDCl_3$) 6.8 (1H, s, aromatic), 3.86 (3H, s, OMe), 3.84 (3H, s, OMe), 2.64 (6H, m), 1.6 (8H, m), 1 (3H, t, CH_3).

5-n-Butyl-7,8-dimethoxy-1,2,3,4-tetrahydro-1-keto-naphthalene oxime : The tetralone (10 g), hydroxylamine hydrochloride (4 g) and sodium hydroxide (3 g) in water (20 ml) were dissolved with addition of alcohol and the mixture was refluxed on a waterbath for 5-6 h. The reaction mixture was then cooled and the precipitated oxime was filtered. The filtrate on concentration gave another crop of oxime. The oxime was recrystallised from dilute alcohol (50%) (8 g, 76%), m.p. 149-50° ; ν_{max} (KBr) 1587 cm^{-1}.

5-Oximino-1-n-butyl-3,4-dimethoxy-6,7,8,9-tetrahydro-5-H-benzocycloheptene : The ketone (3 g) was refluxed on a waterbath with $NH_2OH.HCl$ (3 g), ethanol (30 ml) and pyridine (3 ml) for 2 h. Alcohol was removed, little water added and the separated oil was extracted with ether. Residual viscous oil left after removal of ether was kept in ice chest for three days. The crude mass was purified by crystallisation from petroleum ether (b.p. 60-80°) yield (1.65 g, 52%), m.p. 98-99.5° ; ν_{max} (KBr) 1590 cm^{-1} ; δ($CDCl_3$) 6.72 (1H, s, aromatic) ; 3.88 (3H, s, OMe) ; 3.8 (3H, s, OMe) ; 2.68 (6H, m) ; 1.6 (9H, m) ; 1 (3H, t, CH_3) ; m/e 291 (M^+, 100), 259 (45.5), 243 (34.5), 216 (21).

1-Amino-5-n-butyl-7,8-dimethoxy-1,2,3,4-tetrahydronaphthalene (IV : n = 3, $R_1 = R_2$ = H) *:* The oxime (8 g) was reduced by sodium (8 g) and 100% alcohol (80 ml). The reaction mixture was acidified with HCl, alcohol removed and the aqueous solution basified with sodium hydroxide. The amine was extracted with ether and distilled at b.p. 160°/0.8 mm (5 g, 66%) ; ν_{max} (Film) 3300 cm^{-1}. The hydrochloride was crystallised from benzene-petroleum ether (b.p. 60-80°), m.p. 110°.

5-Amino-1-n-butyl-3,4-dimethoxy-6,7,8,9-tetrahydro-5-H-benzocycloheptene (IV : n = 4, $R_1 = R_2$ = H) *:* It was prepared by the above method, b.p. 163-166°/0.8 mm (30%) ; ν_{max} (Film) 3300 cm^{-1} ; m/e 277 (M^+, 1), 260 (91), 245 (63), 230 (35), 203 (100). The hydrochloride (hygroscopic) was crystallised from petroleum ether-ether mixture, m.p. 90-91°. Picrate was crystallised from ethanol, m.p. 156-157.5°.

5-Dimethylamino-1-n-butyl-3,4-dimethoxy-6,7,8,9-tetrahydro-5-H-benzocycloheptene (IV : n = 4, $R_1 = R_2 = CH_3$) *:* It was prepared from the amine (IV : n = 4, $R_1 = R_2$ = H), formic acid and formaldehyde in the usual way. It boiled at 150-152°/0.4-0.5 mm. Picrate was crystallised from ethanol, m.p. 163-164°.

1-(N-Acetylamino)-5-n-butyl-7,8-dimethoxy-1,2,3,4-tetrahydronaphthalene (IV : n=3, R_1=H, R_2=$COCH_3$) : It was prepared by the interaction of acetyl chloride with amine and crystallised from dil alcohol (84%), m.p. 135° ; ν_{max} (KBr) 3300 (NH), 1650 cm^{-1} (amide CO).

The following amides were prepared (R_2, % yield, m.p. in the order shown) : COC_2H_5, 71, 125° ; COC_3H_7, 70, 110°. The analytical results for these compounds were in good agreement with the calculated values.

1-(5-n-Butyl-7,8-dimethoxy-1,2,3,4-tetrahydro) naphthylethylamine (IV : n=3, R_1=H, R_2=C_2H_5) : The acetylamino compound (IV : n=3, R_1=H, R_2-$COCH_3$; 2 g) was reduced with LAH (0.2 g) in dry ether (150 ml) in the usual way to yield the product (1.6 g), b.p. 180°/1.5 mm ; ν_{max} (film) 3300 cm^{-1} ; picrate (EtOH) m.p. 173°. The following amines (IV) were prepared (R_2, % yield, b.p., m.p. of the picrate in the order shown) : C_3H_7, 76, 165°/0.6 mm, 168° ; C_4H_9, 83, 178°/1 mm, 162°. The analytical results for these compounds were in good agreement with the calculated values.

1-(5-n-Butyl-7,8-dimethoxy-1,2,3,4-tetrahydronaphthyl)dimethylamine (IV : n-3 ; R_1=R_2=CH_3) : The amine (IV : n=3, R_1=R_2=H ; 1.6 g), formic acid (90%, 1.6 g) and formaldehyde (37%, 1.5 ml) were reacted together in the usual way to yield the amine (1.2 g, 68%), b.p. 170°/1.5 mm. The hydrochloride was crystallised from benzene and petroleum ether (b.p. 60-80°) mixture, m.p. 110°.

The following amines (IV : n=3, R_1-CH_3, R_2) were prepared similarly (R_2,% yield, b.p., m.p. of the hydrochloride in the order shown) : C_2H_5, 66, 240°/1.5 mm, 115° (benzene-petroleum ether) ; C_3H_7, 65, 185°/0.6 mm, 118° (benzene-petroleum ether) ; C_4H_9, 62, 135°/0.4 mm, 121° (benzene-petroleum ether).

Pharmacology : In vitro amebicidal activity of IV against *E. histolytica* was carried out at Kalyani University, West Bengal. Minimum inhibitory concentration (μg/ml) of the following compounds (IV) are (n, R_1, R_2, M.I.C in the order shown) : 3, H, H, 15.8 ; 3, CH_3, CH_3, 62.5 ; 3, CH_3, C_2H_5, nil ; 3, CH_3, C_3H_7, nil ; 3, CH_3, C_4H_9, nil ; 4, H, H, 62.5[11] ; 4, CH_3, CH_3, 250.0, while M.I.C. of emetine hydrochloride is 7.87 μg/ml.

From the screening report it appears that the seven membered compounds are less active than the six membered compounds.

Acknowledgement

The authors are thankful to Dr. S. Lahiri, Kalyani University for the test report of antiamebic activity. Financial assistance (B.R.S.) from U.G.C., New Delhi is also gratefully acknowledged.

References

1. R. CHILD and F. L. PYMAN, *J. Chem. Soc.*, 1929, 2010.
2. F. L. PYMAN, *Chem. Ind. (London)*, 1937, **56**, 789.
3. L. G. GOODWIN, C. A. HOARE and T. M. SHARP, *Br. J. Pharmacol.*, 1948, **3**, 44, 68.
4. J. M. OSBOND, *J. Chem. Soc.*, 1951, 3464 ; 1952, 4785.
5. D. HALL MURIEL, S. MAHBOOB and E. E. TURNER, *J. Chem. Soc.*, 1950, 1842 ; 1952, 149.
6. S. MAHBOOB and M. L. DHAR, *J. Sci. Ind. Res. Sect. B*, 1955, **14**, 1.
7. C. N. KACHRU and B. PATHAK, *J. Indian Chem. Soc.*, 1957, **34**, 611, 768.
8. B. S. KAUSHIVA, *J. Sci. Ind. Res. Sect. C*, 1957, **16**, 224.
9. H. N. SHARMA and C. N. KACHRU, *J. Indian Chem. Soc.*, 1959, **36**, 371.
10. Personal communication.
11. S. DUTTA, A. PAL, B. P. DEY and S. C. LAHIRI, *J. Indian Chem. Soc.*, 1982, **59**, 902.
12. H. N. SHARMA and C. N. KACHRU, *Curr. Sci.*, 1959, **8**, 327.

Studies on Antitubercular and Antibacterial Agents : Preparation of 1-(4-Amino benzoyl)-2-benzalhydrazine and 1-[4-(phenylthioureido)benzoyl]-2-substituted-benzalhydrazine

J. M. PATEL, M. P. DAVE, N. A. LANGALIA

and

K. A. THAKER

University Department of Chemistry, Bhavnagar University, Bhavnagar-364 002

Manuscript received 6 June 1983, revised 28 December 1983, accepted 26 May 1984

LITERATURE reveals that a number of studies have been carried out on antitubercular and antibacterial activity of hydrazone and thiourea. Hydrazones have also been found to possess antibacterial[1,2], antifungal[3] and insecticidal[4,5] activities. A number of hydrazones have been synthesised through condensation of acid hydrazide with aldehyde and ketone.

The thioureas with various structural modifications are tuberculostatic[6,7], anthelmintics[8], antifungal[9] and rodenticides[10]. We have prepared 1-[4-(phenylthioureido)benzoyl]-2-substituted-benzalhydrazine from various 1-(4-aminobenzoyl)-2-benzalhydrazine by condensation with phenylisothiocynate and tested against $H_{37}R_v$ strain of *Mycobacterium tuberculosis*.

The synthetic sequence of the title compounds is obtained in Scheme 1.

Experimental

4-Aminobenzhydrazide : It was prepared by the reported method[11].

1-(4-Aminobenzoyl)-2-benzalhydrazine (II) : To the solution of 4-aminobenzhydrazide (0.01 *M*) in ethanol (95%, 25 ml) added benzaldehyde (0.01 *M*) in ethanol (95%, 15 ml), content kept for 24 h at room temperature, cooled, filtered, dried and crystallised

TABLE 1—DATA OF THE 1-(4-AMINOBENZOYL)-2-BENZAL HYDRAZINE (I)

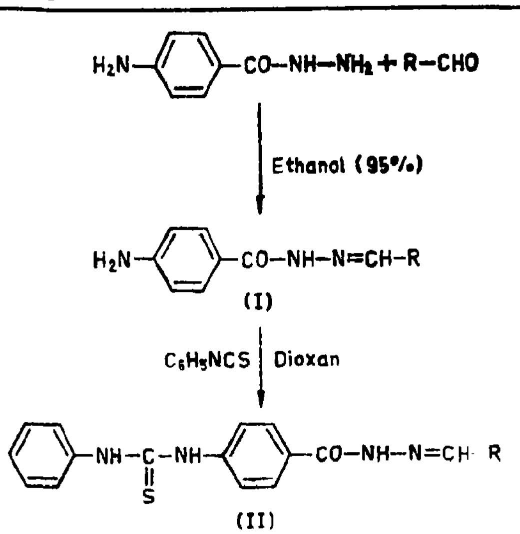
Sl. no.	R	M.p. °C	Yield %	Antitubercular activity, µg/ml 0.0	25	50	100	150	Antibacterial activity Interpretation of zone of inhibition S. aureus	E. coli
1.	Phenyl	211	87	+	+	+	+	+	–	–
2.	2-Hydroxyphenyl	210	89	+	–	–	–	–	++	–
3.	4-Hydroxyphenyl	250	90	+	–	–	–	–	+	+
4.	Cinnamyl	170	81	+	+	+	+	+	–	–
5.	4-Methoxyphenyl	215	88	+	–	–	+	+	–	–
6.	2-Chlorophenyl	161	84	+	+	+	+	+	–	–
7.	3-Chlorophenyl	225	80	+	+	+	+	–	+	–
8.	3-Nitrophenyl	218	79	+	+	+	+	+	+	+
9.	4-Nitrophenyl	290	75	+	+	+	+	+	+	–
10.	3,4-Methylenedioxyphenyl	266	87	+	–	–	+	+	–	–
11.	4-Hydroxy-3-methoxyphenyl	128	90	+	+	+	–	–	–	+
12.	3,4-Dimethoxyphenyl	252	79	+	+	+	+	+	–	–
13.	3,5-Dibromo-2-hydroxyphenyl	257	88	+	–	–	+	–	+	–
14.	5-Bromo-2-hydroxyphenyl	245	89	+	–	–	–	–	+	–
15.	5-Nitro-4-hydroxy-3-methoxyphenyl	222	79	+	+	+	+	+	–	–
16.	Furfuryl	187	76	+	+	+	+	+	–	–

All the compounds gave satisfactory C, N, S analyses.
For antitubercular activity : +ve=not active ; –ve=active.
For antibacterial activity : +ve=active ; –ve=not active.

TABLE 2—DATA OF THE 1-[4-(PHENYLTHIOUREIDO)-BENZOYL]-2-BENZAL HYDRAZINE (II)

Sl. no.	R	M.p. °C	Yield %	Antitubercular activity, µg/ml 0.0	25	50	100	150	Antibacterial activity Interpretation of zone of inhibition S. aureus	E. coli
1.	Phenyl	172	80	+	+	+	+	+	–	–
2.	2-Hydroxyphenyl	295	86	+	–	–	+	+	+	+
3.	4-Hydroxyphenyl	168	88	+	–	–	–	–	+	–
4.	Cinnamyl	176	76	+	+	+	+	+	–	–
5.	4-Methoxyphenyl	195	82	+	+	+	+	+	–	–
6.	2-Chlorophenyl	178	81	+	–	–	+	+	–	–
7.	3-Chlorophenyl	228	72	+	–	–	+	+	–	–
8.	3-Nitrophenyl	150	76	+	+	+	+	+	+	–
9.	4-Nitrophenyl	154	71	+	+	+	+	+	–	–
10.	3,4-Methylenedioxyphenyl	175	78	+	+	+	–	–	–	–
11.	4-Hydroxy-3-methoxyphenyl	199	84	+	+	+	+	+	–	–
12.	3,4-Dimethoxyphenyl	110	75	+	+	+	+	+	–	+
13.	3,5-Dibromo-2-hydroxyphenyl	232	83	+	–	–	+	+	+	+
14.	5-Bromo-2-hydroxyphenyl	164	80	+	–	–	+	+	+	+
15.	5-Nitro-4-hydroxy-3-methoxyphenyl	150	74	+	+	+	+	+	–	–
16.	Furfuryl	208	72	+	+	+	+	+	–	–

Explanation same as in Table 1.



Scheme 1

where R = Different aromatic, heterocyclic group.

from ethanol (95%), (87%), m.p. 211° (Found : N, 17.42%. $C_{14}H_{18}N_3O$ requires N, 17.57%).

1-[4-(Phenylthioureido)benzoyl]-2-benzalhydrazine (II) : To the solution of 1-(4-aminobenzoyl)-2-benzalhydrazine (0.01 *M*) in dioxan (40 ml) added phenylisothiocynate (0.01 *M*) in dioxan (15 ml), contents refluxed for 45 min, cooled and filtered. The product was washed with ether and crystallised from ethanol (95%), (78%), m.p. 172° (Found : N, 14.85 ; S, 8.45%. $C_{21}H_{18}N_4OS$ requires N, 14.9 ; S, 8.55%).

Antimycobacterial screening : The *in vitro* antitubercular activity of the title compounds **I** and **II** was studied at 0, 25, 50, 100, 150 µg/ml concentration (solvent DMF) against $H_{37}R_v$ strain of *Mycobacterium tuberculosis* using Lowenstein-Jensen medium. The procedure was duplicated with the solvent for control purpose.

Antibacterial screening : The antibacterial activity of the title compounds **I** and **II** was studied

against *E.coli* and *S. aureus*. The disk concentration of 100 μg/disk of all the compounds have been prepared using DMF as solvent.

The physical data of the compounds are recorded in Table 1 and 2. The ir spectra of thiourea, where R=2-hydroxyphenyl show band at 1380 cm^{-1} due to –NH–CS–NH– linkage and characteristic band at 3200 cm^{-1} suggesting the presence of stretching vibration of OH group of salicylaldehyde moiety.

Acknowledgement

The authors are thankful to Bhavnagar University for research facilities and research scholarships (J.M.P. and M.P.D.) and to Dr. S. B. Trivedi, Director, Tuberculosis Research Centre, Amargadh for antitubercular and antibacterial testing facilities.

References

1. P. MONTEGAZZA, F. PACCHIANE and G. CAVALIND, *Antibiot. Chemother.*, 1961, **11**, 405.
2. R. H. WILEY and R. L. OLEVENGER, *J. Med. Pharm. Chem.*, 1962, 5, 1367.
3. A. N. COST, A. A. SHUMAKOVA, E. I. KOZOLOVA and L. I. GANDBERG, *Chem. Abstr.*, 1960, **54**, 14553.
4. G. T. BOTTGER, A. P. YERINGTON and S. I. GERTLER, *Chem. Abstr.*, 1951, **45**, 6336.
5. W. R. ADDER and D. P. GRIGHT, U. S. Pat. 3157569/1962.
6. J. D. BROOKS, P. T. CHARLTON, P. E. MACEY, D. A. PEAK and W. F. SHORT, *J. Chem. Soc.*, 1950, 452.
7. G. HAGELLOCK and K. LIEBERMEISTER, *Z. Naturforsch, Teil B*, 1951, 6, 147.
8. Brit. Pat., 30192, *Chem. Abstr.*, 1918, 12, 1051.
9. M. SHIMOTANI, *J. Pharm. Soc. Jpn.*, 1952, **72**, 328, 9.9.
10. A. BRAIN, *Arch. Intern. Pharmadyamine*, 1949, **80**, 801.
11. M. OLEASON, P. VAN and H. VENDERHAEGHE, *J. Pharm. Pharmacol.*, 1954, 6, 127.

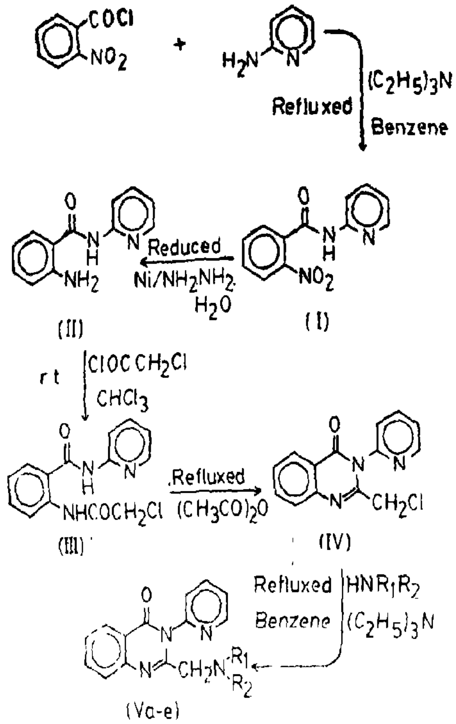
Possible Antifertility Agents. Part-I. Synthesis of 2-(*N,N*-Substituted-aminomethyl)-3-(2-pyridyl)-4(3*H*)-oxo-3,1-quinazolines

Y. D. KULKARNI*, S. H. R. ABDI and V. L. SHARMA

Department of Chemistry, University of Lucknow, Lucknow-226 007

Manuscript received 9 September 1983, revised 2 June 1984, accepted 17 June 1984

SEVERAL quinazoline-4-one derivatives have been reported[1-3] to exhibit appreciable antifertility activity. Similarly, other heterocyclic systems with basic amine residues were also reported[4-6] to exert antifertility action. Therefore, it was considered worthwhile to synthesise 2-(*N,N*-substituted aminomethyl)-3-(2-pyridyl)-4(3*H*)-oxo-3,1-quinazolines which incorporated these structural features (Scheme I) and to study their antifertility action.



Scheme I

Experimental

M.ps. were determined in open capillary tubes and uncorrected. Infrared spectra of the compounds were recorded on a Perkin Elmer 137 infracord and Perkin Elmer 177 grating instruments. The pmr spectra were recorded on Perkin Elmer R-3 spectrometer (90 MHz) in $CDCl_3$ and the chemical shift values are expressed in δ units using TMS as an internal standard.

2-Nitro-benz(2-pyridyl)amide (*I*) : 2-Aminopyridine (1.88 g, 0.02 mol) and 2-nitrobenzoyl chloride (3.71 g, 0.02 mol) were refluxed in dry benzene in presence of triethylamine (6 ml, 0.04 mol) for 10 h (tlc). Triethylamine hydrochloride separated out was filtered and the filtrate on concentration yielded the crude amide which was recrystallised from ethanol (3.0 g, 62%), m.p. 150-52° (Found : N, 17.29%. $C_{12}H_9N_3O_3$ requires N, 17.28%) ; ν_{max} (KBr) 1350 and 1535 (N=O), 1595 (C=C), 1700 (C=O) and 3400 cm^{-1} (NH stretching).

2-Amino-benz(2-pyridyl)amide (**II**) : Hydrazine hydrate (40 ml) was carefully added to a solution of amide (**I**) (2.40 g, 0.01 mol) in methanol (50 ml) containing Raney nickel (0.5 g) for 4 h at room temperature. Then catalyst was filtered off and the filtrate was concentrated to obtain the product (1.5 g, 70%), m.p. 130-31° (lit.[7] 132-33°) (Found : N, 19.75%. $C_{12}H_{11}N_3O$ requires N, 19.72%) ; ν_{max} (KBr) 1595 (C=C), 1680 (C=O) and 3300, 3400 cm^{-1} (NH). The absence of peaks at 1380 and

1535 cm^{-1} (NO_2) further confirmed the complete reduction of the compound I.

*2-N-Chloroacetylamino-benz(2-pyridyl)amide(***III***)* : To a solution of amino compound (**II**) (1.07 g, 0.005 mol) in 50 ml chloroform, chloroacetyl chloride (0.75 ml, 0.01 mol) was added and left overnight at room temperature. Reaction mixture was concentrated under reduced pressure which upon cooling yielded the product (1.0 g, 69%), m.p. 220-22°d. (Found : N, 14.54%. $C_{14}H_{12}ClN_3O_2$ requires N, 14.51%) ; ν_{max} (KBr) 760 (C−Cl), 1595 (C=C), 1640 (C=O), 1680 (C=O), and 3100 cm^{-1} (NH).

2-Chloromethyl-3-(2-pyridyl)-4(3H)-oxo-3,1-quinazoline (**IV**) : A solution of **III** (0.58 g, 0.002 mol) in 10 ml of acetic anhydride was refluxed for 7.5 h (tlc). The reaction mixture was poured over crushed ice and the solid separated was filtered and washed with water. The crude product was recrystallised from benzene/petroleum ether (b.p. 60-80°) (1 : 1) (0.36 g ; 60%) m.p. 175-76° (Found : N, 15.44%. $C_{14}H_{11}ClN_3O$ requires N, 15.47%) ; ν_{max} (KBr) 760 (C−Cl), 1595 (C=C), 1700 (C=O) and 2950 cm^{-1} (C−H methyl).

2-(N,N-Substituted aminomethyl)-3-(2-pyridyl)-4(3H)-oxo-3,1-quinazoline (**Va-e**) : The chloro compound **IV** (0.543 g, 0.002 mol) and an appropriate secondary amine (0.0025 mol) were refluxed in 25 ml pyridine for 6-8 h (tlc). The excess of pyridine was distilled off under reduced pressure and the residue poured over crushed ice. The crude product thus separated was filtered, dried and recrystallised from aqueous ethanol. The compounds were characterised by their elemental analysis, m.ps., pmr spectra and the absence of C−Cl band at 760 cm^{-1} in their ir (KBr) spectra.

Biological screening : Method of Kamboj *et al.*[8] was used to evaluate anti-implantation activity. However, none of these compounds showed any significant activity at an oral dose level of 25 mg/kg body weight.

TABLE 1

Compd. no.	NR_1R_2	Molecular formula	M.p. °C
Va	diethylamino-	$C_{18}H_{20}N_4O$	304-06
Vb	pyrrolidino-	$C_{18}H_{18}N_4O$	294-96
Vc	piperidino-	$C_{19}H_{20}N_4O$	292-94
Vd	4-methyl-piperidino-	$C_{20}H_{22}N_4O$	282-84
Ve	morpholino-	$C_{18}H_{18}N_4O_2$	298-300

Acknowledgement

The authors wish to thank Head of the Chemistry Department, Lucknow University, for laboratory facilities, Director, C.D.R.I., Lucknow for providing spectral data and antifertility screening facilities and the U.G.C., New Delhi for financial assistance to one of the authors (S.H.R.A.).

References

1. S. K. SAXENA and A. S. NADKARNI, *Indian J. Med. Res.*, 1971, **59**, 1109.
2. R. G. BOUGH, M. R. GURD, J. E. HALL and B. LESSEL, *Nature (London)*, 1963, **200**, 4907.
3. J. D. McCOLL, S. ROBSON and M. GLOBUS, *Toxicol. Appl. Pharmacol.*, 1967, **10**, 244.
4. M. S. MANHAS, W. A. HOFFMAN III and A. K. BOSE, *J. Heterocycl. Chem.*, 1979, **16**, 711.
5. P. K. GROVER, H. P. S. CHAWLA, N. ANAND, V. P. KAMBOJ and A. B. KAR, *J. Med. Chem.*, 1965, **8**, 720.
6. R. R. CRENSHAW, A. T. JEFFRIES, G. M. LUCKE, L. C. CHENEY and G. BIALY, *J. Med. Chem.*, 1971, **14**, 1185.
7. R. H. CLARK and E. C. WAGNER, *J. Org. Chem.*, 1944, **9**, 55.
8 V. P. KAMBOJ, A. B. KAR, R. GOPALACHARI and R. N. IYER, *Indian J. Exptl. Biol.*, 1975, **13**, 79.

Possible Antifertility Agents. Part-II : Synthesis of 10,12-Substituted [1,4]-benzoxazino [3,4]-quinazolin-8-ones

Y. D. KULKARNI* and S. H. R. ABDI

Department of Chemistry, University of Lucknow, Lucknow-226 007

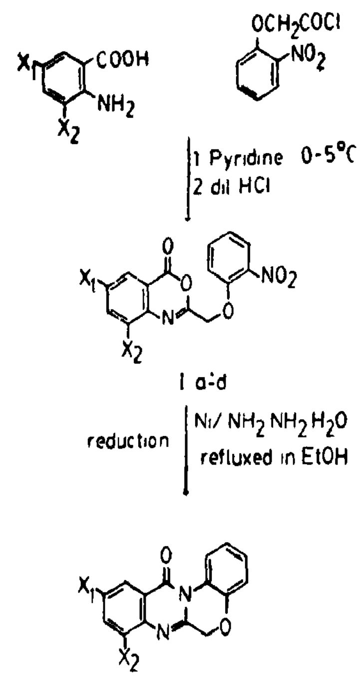
Manuscript received 12 September 1983, revised 2 June 1984, accepted 17 June 1984

HIGH antifertility activity has been located among certain benz[a]anthracene derivatives[1] and also in substituted quinazolones[2-4]. Therefore, it was considered worthwhile to synthesise substituted [1,4]-benzoxazine [3,4]-quinazolin-8-ones which incorporated the essential structural skeleton of both classes of the compounds (Scheme 1) and to study their antifertility action.

Experimental

M.ps. were determined in open capillary tubes and uncorrected. Infrared spectra of the compounds were recorded on the Perkin Elmer 137 infracord instrument and the pmr spectra was recorded on the Perkin Elmer R-3 spectrometer (90 MHz) in trifluoroacetic acid and the chemical shift values were expressed in δ units using TMS as an internal standard.

2-(2-Nitrophenoxy methyl)-6,8-substituted-4(3H)-oxo-3,1-benzoxazines (**Ia-d**) : The compounds were synthesised according to the method of Sammour *et al*[5]. 2-Nitrophenoxyacetic acid[6] (2.98 g, 0.01 mol) was refluxed with a large excess of thionyl chloride for 6 h. Excess of thionyl chloride was distilled off and its traces were removed by the azeotropic distillation with dry benzene (3 times). The acid chloride obtained was allowed to react with appropriate anthranilic acid (0.01 mol) in 10 ml dry pyridine at 0-5° for 1 h. The reaction mixture was kept overnight at room temperature and treated with cold dilute hydrochloric acid. The separated solid was filtered, washed with sodium bicarbonate solution and finally with water. The crude product was recrystallised from ethanol (Table 1).



Scheme 1

TABLE 1

Compd. no.	X_1	X_2	Molecular formula	M.p. °C	Yield %
Ia	H	H	$C_{15}H_{10}N_2O_5$	209-10	50
Ib	Br	H	$C_{15}H_9N_2O_5Br$	175-77	90
Ic	Br	Br	$C_{15}H_8N_2O_5Br_2$	162-63	60
Id	I	H	$C_{15}H_9N_2O_5I$	196-97	90

10,12-Substituted [1,4]-benzoxazino [3,4]-quinazolin-8-ones (**IIa-d**) : Benzoxazine (**Ia-d**, 0.01 mol) was dissolved in ethanol (20 ml) and Raney nickel (0.5 g) was placed into it. Hydrazine hydrate (10 ml) was then carefully added at room temperature and after the evolution of hydrogen ceased the reaction mixture was allowed to reflux on a water bath for 3 h. It was then acidified with hot 5 *N* hydrochloric acid and filtered hot. Filtrate on cooling yielded the crude product which was recrystallised from ethanol (Table 2). Absence of the bands

TABLE 2

Compd. no.	X_1	X_2	Molecular formula	M.p. °C	Yield %
IIa	H	H	$C_{15}H_{10}N_2O_2$	155-56	60
IIb	Br	H	$C_{15}H_9N_2O_2Br$	166-67	65
IIc	Br	Br	$C_{15}H_8N_2O_2Br_2$	164-65	55
IId	I	H	$C_{15}H_9N_2O_2I$	165-66	65

in ir (KBr) at 1360 and 1525 cm^{-1} due to the aromatic nitro group present in its precursor indicated that the reduction of nitro group was complete and also the absence of 3300-3400 cm^{-1} band confirmed that the amino group formed during this reduction had reacted intramolecularly with benzoxazine carbonyl group to form the desired product.

Biological screening : The method of Kamboj *et al*[7]. was adopted to evaluate the anti-implantation activity. Compounds were found to have an activity range between 12.5-37.5% only at a dose level of 25 mg/kg body weight of the animal.

Acknowledgement

The authors wish to thank the Head of the Chemistry Department, Lucknow University, for laboratory facilities, Director, C.D.R.I., Lucknow for providing spectral data and antifertility screening facilities and the U.G.C., New Delhi for financial assistance to one of the authors (S.H.R.A.).

References

1. E. M. Charles, K. S. Dilip, L. S. Sara, E. B. Robert and D. Jean, *J. Med. Chem.*, 1982, **25**, 323.
2. S. K. Saksena and A. S. Nadkarni, *Indian J. Med. Res.*, 1971, **59**, 1109.
3. J. D. McColl, S. Robson and M. Globus, *Toxicol. Appl. Pharmacol.*, 1967, **10**, 244.
4. R. G. Bough, M. R. Gurd, J. E. Hall and B. Lessel, *Nature (London)*, 1963, **200**, 4907.
5. A. Sammour, A. F. M. Fahmy and M. Mahmood, *Indian J. Chem.*, 1973, **11**, 222.
6. Ö. Behaghel, *J. Prakt. Chem.*, 1926, **27**, 114.
7. V. P. Kamboj, A. B. Kar, R. Gopalachari and R. N. Iyer, *Indian J. Exptl. Biol.*, 1975, **13**, 79.

Synthesis and Antibacterial Activity of Azomethines and Thiazolidinones Derived from 2-Phenyl-3-(*p*-aminodiphenyl)-4-quinazolones

R. K. SAKSENA* and PADAM KANT

Department of Chemistry, D.A.V. College, Kanpur

Manuscript received 3 October 1983, revised 4 May 1984, accepted 21 July 1984

QUINAZOLONES[1-5] and azomethines/Schiff's[6,7] bases are reported to exhibit a wide spectrum of biological activities. Thiazolidinones also possess a variety of pharmacological properties, *viz.* amoebicidal[8], hypnotic[9], anticonvulsant[10], fungicidal[11] and antibacterial[12]. In view of these observations we thought it of interest to synthesise and investigate the azomethines having a quinazolone nucleus and compounds containing the quinazolone and thiazolidinone moieties in a single molecular frame work as possible antibacterial agents.

2-Phenyl-3-(*p*-aminodiphenyl)-4-quinazolone[13] (I) was refluxed with different arylaldehydes in absolute alcohol in presence of few drops of acetic acid to

TABLE 1—ANALYTICAL AND ANTIBACTERIAL DATA OF 2-PHENYL-3-(p-ARYLIDENEAMINODIPHENYL)-4-QUINAZOLONE (II)

Sl. no.		M.p. °C	Antibacterial activity*				
			S. aureus	*B. pumilis*	*B. subtilis*	*B. branchiseptica*	*S. lutea*
IIa	2-Furyl	>250	++	+++	+++	+	+++
IIb	4-*N*,*N*-Diethylphenyl	289	++	+++	+++	++	++++
IIc	4-*N*,*N*-Dimethylphenyl	282	++	+++	+++	+	++++
IId	2-Hydroxyphenyl	234	++	+++	+++	+	+++
IIe	3-Hydroxy-4-methoxyphenyl	235	++	+++	+++	+	++++
IIf	4-Nitrophenyl	215	++	+++	+++	+	++++
IIg	Phenyl	280	++	+++	+++	++	++++
IIh	4-Hydroxyphenyl	298	++	+++	+++	++	++++

All compounds gave satisfactory C, H analyses.

* Zone size : + = 6-8 mm, ++ = 9-16 mm, +++ = 17-25 mm, ++++ = >26 mm.

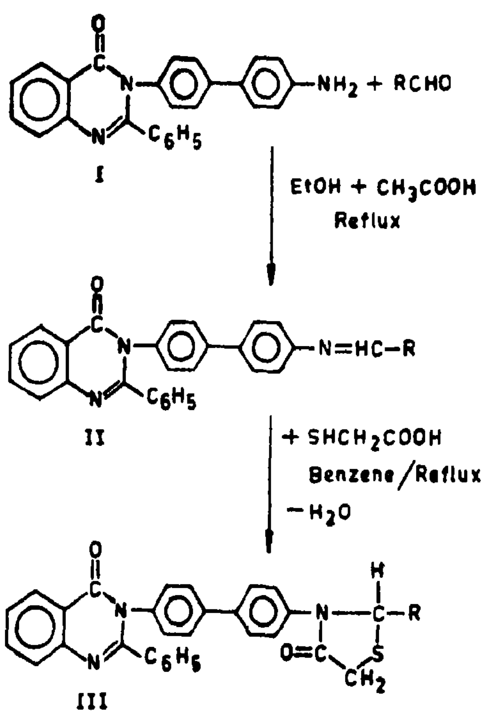
TABLE 2—ANALYTICAL AND ANTIBACTERIAL DATA OF 2-PHENYL-3-p(2-ARYL-4-OXO-THIAZOLIN-3-YL)-DIPHENYL-4-QUINAZOLONE (III)

Sl. no.	R	M.p. °C	Antibacterial activity*				
			S. aureus	*S. pumilis*	*S. subtilis*	*B. branchiseptica*	*S. lutea*
IIIa	2-Furyl	>250	++	++++	+++	–	+++
IIIb	4-*N*,*N*-Diethylphenyl	242	++	++++	+++	–	++++
IIIc	4-*N*,*N*-Dimethylphenyl	218	++	+++	+++	–	+++
IIId	2-Hydroxyphenyl	244	++	+++	+++	–	+++
IIIe	3-Hydroxy-4-methoxyphenyl	266	++	+++	+++	–	++++
IIIf	4-Nitrophenyl	270	++	+++	+++	–	++++
IIIg	Phenyl	225	++	+++	+++	–	++++
IIIh	4-Hydroxyphenyl	201	++	++++	+++	–	++++

All compounds gave satisfactory C, H analyses.

* Zone size : – = No inhibition, + = 6-8 mm, ++ = 9-16 mm, +++ = 17-25 mm, ++++ = >26 mm.

get the desired 2-phenyl-3-(*p*-arylideneaminodiphenyl)-4-quinazolones (**II**), which were reacted with thioglycolic acid to furnish 2-phenyl-3-*p*(2-aryl-4-oxo-thiazolin-3-yl)diphenyl-4-quinazolones (**III**). Structure of compounds **II** and **III** were characterised by their elemental analyses and ir spectra. Compound **II** gave peaks at 1640 ($-\overset{O}{\overset{\|}{C}}-N$) and 1680-1670 cm^{-1} (N=CH-azomethine linkage), whereas compound **III** gave peaks at 1650-1585 (C=O), 1600-1610 (C=C aromatic), 1420-1520 (C-N stretching), 1250-1350 (C-S-C) and 745-820 cm^{-1} (substituted benzene).



I, II, III

Experimental

Infrared spectra (KBr) were recorded on a Perkin-Elmer 377 spectrophotometer. Melting points were determined in a sulphuric acid bath in open capillary. Tlc was done on silica gel plates.

2-Phenyl-3-(p-aminodiphenyl)-4-quinazolone (**I**) : It was obtained in good yield by the reported method[13].

2-Phenyl-3-(p-arylideneaminodiphenyl)-4-quinazolone (**II**) : A mixture of **I** (0.01 mol), arylaldehyde (0.01 mol), ethanol (25 ml) and glacial acetic acid (0.5 ml) was refluxed for 5-6 h. The resulting mixture was cooled and poured over crushed ice. The coloured solid product obtained was washed several times with water and then recrystallised from ethanol. The compounds are recorded in Table 1.

2-Phenyl-3-p(2-aryl-4-oxo-thiazolin-3-yl)diphenyl-4-quinazolone (**III**) : Thioglycolic acid (0.015 mol)

was added to a well stirred solution of II (0.05 mol) in dry benzene/dioxane (50 ml). The mixture was refluxed for 4 h. The excess solvent was removed and the solid mass washed with aqueous sodium carbonate solution (10%) and finally recrystallised from petroleum ether or benzene. The melting points and other data of the compounds are recorded in Table 2.

Antibacterial screening : Agar plate diffusion technique[14] was employed for the determination of antibacterial activity of the synthesised compounds of type II and III against *Staphylococcus aureus, Bacillus pumilus, Bacillus subtilis, Bascillus branchiseptice*, and *Sarcina lutea*. The results are given in Table 1 and 2.

The antibacterial activity of both the series seems to be sporadic with no apparent pattern and thus making it difficult to correlate with structural requirements.

Acknowledgement

Authors are thankful to Dr. H. S. Sodhi, for providing facilities and to U.G.C., New Delhi for financial support.

References

1. R. C. Arora, V. K. Rastogi, A. K. Agarwal and S. S. Parmar, *J. Heterocycl. Chem.*, 1978, **15**, 869.
2. M. Sharma, K. Shanker, K. P. Bhargava and K. Kishore, *Indian J. Pharm. Sci.*, 1979, **41**, 49.
3. G. Doria, C. Romeo, P. Sberze, M. Tibolla, M. L. Corno and G. Chdelli, *Eur. J. Med. Chem.*, 1979, **14**, 247.
4. A. K. Sengupta and H. Misra, *J. Pharm. Sci.*, 1980, **69**, 1313.
5. A. Berzchet and S. Botkanu, *Farmacia* (*Bucharest*), 1971, **19**, 683 (*Chem. Abstr.*, 1973, **78**, 131908).
6. S. Sengupta, *Indian J. Appl. Chem.*, 1966, **29**, 33.
7. F. D. Popp, *J. Org. Chem.*, 1961, **26**, 1566.
8. A. R. Surrey and R. A. Cutler, *J. Am. Chem. Soc.*, 1958, **80**, 578.
9. J. Doran and H. A. Sonle, *J. Org. Chem.*, 1938, 3, 193.
10. H. D. Troutman and L. M. Long, *J. Am. Chem. Soc.*, 1948, **70**, 3436.
11. M. K. Raut and G. N. Mahapatra, *J. Am. Chem. Soc.*, 1955, **77**, 2497.
12. S. V. Patel, N. Y. Nagar and G. B. Joshi, *J. Indian Chem. Soc.*, 1983, **60**, 304.
13. B. Dash, B. K. Dora and C. S. Panda, *J. Indian Chem. Soc.*, 1980, **57**, 835.
14. R. S. Verma, S. A. Iman and W. L. Nobles, *J. Pharm. Sci.*, 1973, **62**, 140.

Synthesis and Antimicrobial Evaluation of 1-(Phenyl/methylcarbamoyloxyphenyl)-2-methyl/phenyl-4-(substituted benzylidene)-5-imidazolone, A New Class of Carbamates†

ANIL K. SENGUPTA* and ANURAG ATEET GUPTA**

Department of Chemistry, Lucknow University, Lucknow-226 007

Manuscript received 14 March 1984, revised 12 June 1984, accepted 17 June 1984

A number of 1-(hydroxyphenyl)-2-methyl/phenyl-4-(substituted benzylidene)-5-imidazolone and their *N*-methyl and *N*-phenyl carbamates have been synthesised and evaluated for their antimicrobial activities against a number of bacteria and fungi.

The biological properties associated with *N*-methyl, *N,N*-dimethyl and *N*-phenyl carbamic esters of various alcohols and phenols have been reported[1-4]. In continuation of our interest towards the synthesis of potential antimicrobial agents[5,6], we hereby report the synthesis of the title carbamates according to the sequence of reaction outlined in Chart 1 with a view to study their antimicrobial efficacy. The choice of imidazolone derivatives arose because their number of analogues have been shown to exhibit diverse types of biological activities including antibacterial properties.

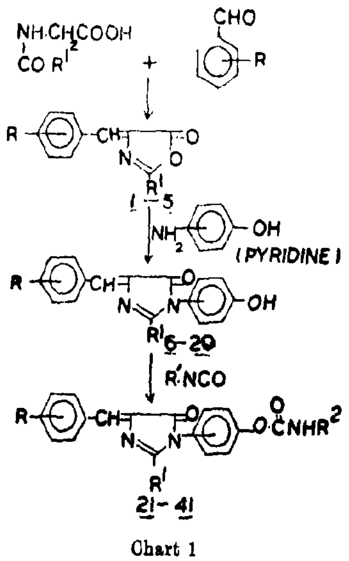


Chart 1

Various 2-methyl/phenyl-4-(substituted benzylidene)-5-oxazolone (**1-5**), obtained by the condensation of acetyl/benzoylglycine with several aryl aldehydes, on reaction with various aminophenols in pyridine, furnished 1-(hydroxyphenyl)-2-methyl/

** Research Officer, Product Development Division, Indian Oil Corporation Ltd., Research and Development Centre, Sector-13, Faridabad-121 007.

† Presented before the Fifth International Congress of Pesticide Chemistry, Kyoto, Japan, 1982.

phenyl-4-(substituted benzylidene)-5-imidazolones (**6-20**). The ir spectra of **6-20** showed strong bands at 1650-1640 (C=N), 1690 (C=O) and 3225 cm^{-1} (OH). The pmr spectrum of **8** showed signals at 7-34-7.75 (m, 9H, ArH), 6.70 (s, 1H, PhCH=), 2.24 (s, 3H, CH_3) and 8.20 (s, 1H, OH, exchangeable with D_2O), whereas a thirteen proton multiplet of compound **19** was observed at 7.00-7.55 along with a singlet of three protons at 3.80, assigned to $-OCH_3$. The spectra and integrations are consistent with the proposed structures.

Refluxing **6-20** with methyl/phenyl isocyanate in dry benzene or THF in presence of triethylamine yielded the title carbamates (**21-41**). The ir spectra showed bands at 1680 (C=O of imidazoline), 1700-1690 (C=O of CONH), 1645 (C=N of imidazolone) and 3320 cm^{-1} (NH). The pmr spectrum of **29** showed signals at 7.25-7.68 (m, 19H, ArH), 6.8 (s, 1H, PhCH=), 12.25 (m, 1H, NHCO, exchangeable with D_2O). The spectrum was featureless in the methyl and methylene proton region. Additional signals in the methyl region at 3.82 and 2.78, in the spectrum of **37**, were assigned to OCH_3 and $N-CH_3$ protons. In the spectrum of **23**, a pair of three proton signals at 2.36 (s) and 2.82 (d) were assigned to CH_3X_2 protons in different chemical environment.

Table 1—1-(Hydroxyphenyl)-2-methyl/phenyl-4-(substituted benzylidene)-5-imidazolones (**6-20**)

Compd. no.	R	R¹	Position of heterocyclic	M.p. °C
6	H	CH_3	2	119
7	H	CH_3	3	157-8
8	H	CH_3	4	128
9	H	C_6H_5	2	141
10	H	C_6H_5	3	214
11	H	C_6H_5	4	219
12	p-Cl	CH_3	2	129
13	p-Cl	CH_3	3	187
14	p-Cl	CH_3	4	249-50
15	p-Cl	C_6H_5	2	199
16	p-Cl	C_6H_5	3	245-6
17	p-Cl	C_6H_5	4	287-8
18	p-OCH_3	C_6H_5	2	236
19	p-OCH_3	C_6H_5	3	238-9
20	p-OCH_3	C_6H_5	4	259-60

Compounds no. **1, 2, 3, 4, 5, 8, 12, 13** recrystallised for methanol; **6, 7, 10, 11, 14** recrystallised for methanol/water; **9** and **15** purified by dissolving in 4 *N* NaOH and precipitating with 2 *N* HCl.

Compounds no. **1** and **4** prepared by both the methods were identical (m.p., m.m.p., ir and ca tlc). Others were obtained by method A only.

All the compounds gave satisfactory C, H and N analyses.

Experimental

All melting points are uncorrected. The ir spectra were obtained on a Perkin-Elmer Infracord 137 and pmr spectra on a Varian A-60D instrument using $CDCl_3$ as solvent and TMS as an internal standard (δ scale). The purity of the compounds was checked by tlc on silica gel G plates.

2-Methyl/phenyl-4-(substituted benzylidene)-5-oxazolones (**1-5**) : A suspension of acetyl/benzoyl glycine (0.01 mol) in acetic anhydride (5 ml) was warmed on a sand bath till all the solid dissolved. After cooling, the reaction mixture was poured into absolute ethanol containing anhydrous sodium acetate (3.0 g) and appropriate aldehyde (0.01 mol). The flask was transferred to a water bath and heated for about 4 h. The reaction mixture was cooled and the resulting solid was filtered and recrystallised from CCl_4 or ethyl acetate.

1-(Hydroxyphenyl)-2-methyl/phenyl-4-(substituted benzylidene)-5-imidazolones (**6-20**) :

Method A : A mixture of each of **1-5** (0.01 mol) and respective aminophenol (0.01 mol), in dry pyridine (10 ml), was refluxed on a sand bath for 5-8 h under absolute anhydrous conditions. Excess of pyridine was removed by distillation. The concentrated mass was cooled and dissolved in minimum ethanol and poured in excess of ice-cold water. The solid mass thus obtained was thoroughly washed with cold water, followed by petroleum ether (b.p. 60-80°), filtered and recrystallised from appropriate solvent (Table 1).

Method B : A mixture of each of **1-5** (0.01 mol) and respective aminophenol (0.01 mol) was fused at 160-70° (oil bath) for about 2 h under anhydrous condition. The crude hydroxyphenyl derivatives of imidazolone thus obtained on cooling were recrystallised from appropriate solvent (Table 1).

1-(Phenyl/methylcarbamoylphenyl)-2-methyl/phenyl-4-(substituted benzylidene)-5-imidazolones (**21-41**) : A solution of appropriate phenol (**6-20**) (0.01 mol) in dry benzene or THF was added portion wise to a 5 to 10% excess of phenyl/methyl isocyanate. After the addition was complete, 2-3 drops of triethylamine was added and the mixture was refluxed for a period varying from 2-20 h. The product was isolated by concentration of the reaction mixture *in vacuo* with subsequent agitation of the residue to induce crystallisation. The carbamates were recrystallised from appropriate solvent and their melting points and analytical data are presented in Table 2.

Antimicrobial activity : The *in vitro* antibacterial activity of compounds **6-41** was determined against *B. pumilus*, *S. aureus*, *S. lutea*, *E. coli*, *B. subtilis*, *B. megaterium*, *B. cereus* and *B. polymyxa* at a dose level of 200 μg/0.1 ml following the method of Varma and Imam[7]. Antifungal activity was studied against *H. sativum*, *A. terreus* and *A. niger* at three different concentrations, *viz.* 1 : 1000, 1 : 10000 and 1 : 100000 following the method of Horsfall[8].

The antibacterial activity of these compounds especially **14**, **16**, **19**, **24** and **37** against *B. pumilus* had activity equal to that of standard compounds (sulphonamides and antibiotics) whereas marginal activity of these compounds was obtained against

TABLE 2—1-(PHENYL/METHYLCARBAMOYLOXYMETHYL)-2-METHYL/PHENYL-4-(SUBSTITUTED BENZYLIDENE)-5-IMIDAZOLONES (21-41)

Compd. no.	R	R^1	R^2	Position of heterocyclic	M.p. °C
21	H	CH_3	CH_3	2	103
22	H	CH_3	CH_3	3	122
23	H	CH_3	CH_3	4	118
24	H	C_6H_5	CH_3	2	197
25	H	C_6H_5	CH_3	3	220
26	H	C_6H_5	CH_3	4	231-2
27	H	C_6H_5	C_6H_5	2	154
28	H	C_6H_5	C_6H_5	3	206-7
29	H	C_6H_5	C_6H_5	4	186
30	p-Cl	CH_3	C_6H_5	2	111-2
31	p-Cl	CH_3	C_6H_5	3	193
32	p-Cl	CH_3	C_6H_5	4	142-3
33	p-Cl	C_6H_5	C_6H_5	2	137-8
34	p-Cl	C_6H_5	C_6H_5	3	177
35	p-Cl	C_6H_5	C_6H_5	4	186
36	p-OCH_3	C_6H_5	CH_3	2	140
37	p-OCH_3	C_6H_5	CH_3	3	133
38	p-OCH_3	C_6H_5	CH_3	4	109
39	p-OCH_3	C_6H_5	C_6H_5	2	187-9
40	p-OCH_3	C_6H_5	C_6H_5	3	178-9
41	p-OCH_3	C_6H_5	C_6H_5	4	168

Compounds no. 16, 20 and 25 recrystallised from benzene and the rest from benzene petroleum ether.

All the compounds gave satisfactory C, H and N analyses.

S. aureus and *E. coli*. Out of the compounds evaluated, **14** and **24** showed inhibition against all the bacteria. Regarding antifungal activity, four compounds, *viz.* **23**, **25**, **32** and **38** were effective against *A. terreus*, while only compounds **32** and **41** were effective in inhibiting the growth of *H. sativum*. All the compounds are active at higher concentrations and activity decreases markedly on dilution. Rest of the compounds were not active against any of the three species of fungi.

Acknowledgement

The authors thank the Head, Department of Chemistry, Lucknow University for providing facilities and Dr. S. Sharma of C.D.R.I. for suggestions. One of the authors (A.A.G.) is grateful to C.S.I.R., New Delhi for the award of senior research fellowship.

References

1. H. GYSIN, *Chimia*, 1954, **8**, 205.
2. M. KOLIBENZEN, R. L. METCALF and T. R. FUKUTO, *J. Agric. Food Chem.*, 1954, **2**, 864.
3. R. L. METCALF, T. R. FUKUTO and M. Y. WINTON, *J. Econ. Entomol.*, 1960, **53**, 828.
4. R. L. METCALF, T. R. FUKUTO and M. Y. WINTON, *J. Econ. Entomol.*, 1962, **55**, 889.
5. A. K. SENGUPTA and A. A. GUPTA, *Indian J. Chem., Sect. B*, 1982, **21**, 72.
6. A. K. SENGUPTA, M. M. GUPTA and A. A. GUPTA, *Indian J. Chem., Sect. B*, 1982, **21**, 600.
7. R. S. VARMA and S. A. IMAM, *Indian J. Microbiol.*, 1973, **13**, 45.
8. J. G. HORSFALL, *Bot. Rev.*, 1945, **5**, 357.

Chemical Examination of the Leaves of *Woodfordia fruticosa*

(MRS.) S. DAN* and S. S. DAN

Botanical Survey of India, Calcutta-700 016

Manuscript received 28 May 1981, accepted 30 May 1984

WOODFORDIA fruticosa kurz.[1] (syn. *Woodfordia floribunda* Salisb) (Lythraceae) a beautiful much branched shrub with brilliant scarlet flowers, is very common in North India but scarce in Orissa and South India. Leaves of this plant are used for dying and tanning purposes[2]. Besides, the leaves possess antibiotic[3,4] as well as sedative[5] properties.

The presence of naphthaquinone[6], polyphenols[7] and traces of alkaloid[5] in the leaves were reported earlier. The present communication deals with the isolation and identification of triterpenoids and sterol in the leaves. The plant material (450 g) collected from Similpal forest, Orissa, was exhaustively extracted with rectified spirit in a Soxhlet Extractor. The alcoholic extract was concentrated under reduced pressure. The dark coloured semi-solid mass obtained was separated into ether soluble and ether insoluble parts. Ether soluble part was then separated[8] into acidic and neutral fractions.

The total acid fraction (0.21 g) was chromatographed over silica gel. Elution with $CHCl_3$: methanol (98 : 2) yielded a crystalline material showing one major and another minor spots in tlc (silica gel, $CHCl_3$, visualized with L-B reagent) which were separated by preparative tlc. The major compound on repeated crystallisation from methanol afforded betulinic acid as shining needles (11 mg), m.p. 310-312°. It yielded an acetate as plates, m.p. 291-293°, identical with authentic acetate of betulinic acid[9] (m.p., m.m.p., ir). On methylation with diazomethane it gave a methyl ester (m.p. and m.m.p. 221-222°).

The minor compound was identified as oleanolic acid by comparative tlc with authentic oleanolic acid and by m.p. (308-310°). Further work could not be done due to paucity of material.

Chloroform : methanol (96 : 4) eluted another crystalline material (silica gel, $CHCl_3$: EtOAc 1 : 1, single purple spot with L-B reagent). It crystallised from methanol as needles (92 mg), m.p. 279-282°, $[\alpha]_D + 64°$ (c 0.41 in $CHCl_3$) ; acetate m.p. 289-290°, $[\alpha]_D + 60°$ (c 0.31 in $CHCl_3$) ; methyl ester m.p. 170° identical with authentic methyl ursolate[10] (m.p., m.m.p., ir).

The neutral fraction was chromatographed over neutral alumina. Petroleum ether : benzene (1 : 1) eluted lupeol (100 mg) m.p. 210-211°, $[\alpha]_D + 22°$ (c 2.0 in $CHCl_3$), acetate m.p. 209-211°, $[\alpha]_D + 44°$ (c 0.37 in $CHCl_3$) ; benzoate m.p. 251-61°. Finally the identity was established as lupeol by comparison with authentic lupeol (m.p., m.m.p., ir). Benzene eluted β-sitosterol (38 mg), m.p. 136-137° ; acetate m.p. 128°, $[\alpha]_D - 35°$ (c 0.29 in $CHCl_3$) ; benzoate m.p. 144°. Identity of β-sitosterol was

established by comparison with an authentic specimen (m.p., m.m.p., superimposable ir).

The residue from benzene : $CHCl_3$ (9 : 1) eluates afforded betulin crystallises from benzene-methanol (18 mg), m.p. 253-255° ; acetate m.p. 220-223°, $[\alpha]_D$ +21° (*c* 0.30 in $CHCl_3$). The latter was identical with authentic betulin acetate[11] (m.p., m.m.p., ir).

The leaves of *W. fruticosa* was thus found to contain lupeol (0.023%), β-sitosterol (0.008%), betulin (0.004%), ursolic acid (0.022%), betulinic acid (0.001%) and minute quantity of oleanolic acid.

Acknowledgement

Authors thank Dr. S. K. Jain, Ex-Director, Botanical Survey of India, Howrah for facilities and Dr. S. C. Pakrashi, Deputy Director, Indian Institute of Molecular Biology, Calcutta for instrumental analyses.

References

1. H. H. Haines, "Flora of Bihar and Orissa", Botanical Survey of India, Calcutta, 1960, Vol. II, p. 890.
2. J. F. Duthie, "Flora of Upper gangetic plain", Botanical Survey of India, Calcutta, 1960, Vol. I, p. 323.
3. C. G. Joshi and N. G. Magar, *J. Sci. Ind. Res., Sect. B*, 1952, **11**, 261.
4. M. L. Dhar, M. M. Dhar, B. N. Dhawan, B. N. Mehrotra and C. Ray, *Indian J. Exp. Biol.*, 1968, **6**, 232.
5. R. R. Paris and H. Jacquemin, *Fitoterapia*, 1976, **47**, 51 (*Chem. Abstr.*, 1976, **85**, 149025).
6. A. G. Saoji, A. N. Saoji and V. K. Deshmukh, *Curr. Sci.*, 1972, **41**, 192.
7. A. G. R. Nair, J. P. Kotiyal, P. Ramesh and S S. Subramanian, *Indian J. Pharm.*, 1976, **38**, 110.
8. F. D. Dodge, *J. Am. Chem. Soc.*, 1918, **40**, 1917.
9. S. C. Pakrashi, J. Bhattacharyya, S. Mookerjee, T. B. Samanta, and H. Verbruggen, *Phytochemistry*, 1968, **7**, 465.
10. S. Mookherjea, *J. Indian Chem. Soc.*, 1973, **50**, 69.
11. S. Dan and S. S. Dan, *J. Indian Chem. Soc.*, 1980, **57**, 760.

Chemical Investigation of *Viscum articulatum*

SARMILA RAY, T. N. THAKUR,** AMITABHA GHOSH

and

A. K. BARUA*

Department of Chemistry, Bose Institute, Calcutta-700 009

Manuscript received 28 October 1983, revised 12 June 1984, accepted 21 July 1984

VISCUM articulatum (Loranthaceae) is an epiphyte. No work on the chemical constituents of the plant appears to have been reported in the literature. We now report the result of chemical investigation on this plant.

The plant growing on *Diospyros peregrina* was collected from the district of Hazaribagh, Bihar. Three neutral and two acid triterpenes were isolated from the benzene extract of the air-dried and crushed plant material.

The neutral triterpenes were isolated in pure state from the mixture by repeated tlc over silica gel G impregnated with $AgNO_3$ following the reported method[1]. The triterpenes thus obtained had melting points 186°, 211-212° and 258°, respectively. The compound having m.p. 186° has molecular formula $C_{30}H_{50}O$ (M^+426) ; monoacetate, $C_{32}H_{52}O_2$ (M^+468), m.p. 225°. Its mass spectral peaks at *m/e* 189, 207 and 218 were very similar to those of α-amyrin. The compound was identified as α-amyrin by comparing its m.p., m.m.p., tlc and glc data with an authentic sample. The compound having m.p. 211-212° has molecular formula $C_{30}H_{50}O$ (M^+426) ; monoacetate, $C_{32}H_{52}O_2$ (M^+468), m.p. 213-215°. The compound was identified as lupeol by comparison of its m.p., tlc and glc data with an authentic sample. The compound having m.p. 258° has molecular formula $C_{30}H_{50}O_2$ (M^+442). Its mass spectral peaks at *m/e* 189, 203, 207, 220 and 234 were very similar to those of betulin[2]. The compound was identified as betulin by comparing its m.p., m.m.p., tlc and glc data with an authentic sample.

The two acid triterpenes could be isolated from the mixture by repeated tlc over silica gel G (solvent, $CHCl_3$: petroleum ether (b.p. 60-80°) : HOAc=64 : 33 : 3 v/v]. The acids thus obtained had m.p. 304-308° and 314-316°, respectively. The acid, $C_{30}H_{48}O_3$, having m.p. 304-308° formed a monomethyl ester, $C_{31}H_{50}O_3$ (M^+470), m.p. 199-200°, on treatment with ethereal diazomethane. The mass spectrum of the ester showed characteristic peaks at *m/e* 207 and 262. The acid was identified as oleanolic acid by direct comparison of its m.p., m.m.p., tlc and glc data of its methyl ester with an authentic sample of methyl oleanolate. The second acid, $C_{30}H_{48}O_3$, m.p. 314-316°, formed a monomethyl ester, $C_{31}H_{50}O_3$, m.p. 224-225° (M^+470). The mass spectrum of the methyl ester showed peaks at *m/e* 189 202, 203, 207, 220 and 262, very similar to those of methyl betulinate[3] and was also supported by the nmr spectrum of the methyl ester. Finally, the acid was identified as betulinic acid by comparison of m.p., m.m.p., tlc and glc data of the methyl ester with an authentic sample.

It should be pointed out that mixture of α-amyrin, lupeol and betulin and also oleanolic acid, ursolic acid and betulinic acid are of common occurrence in the plant kingdom. Separation of individual constituents from above type of mixture even by preparative tlc is difficult and time-consuming. This can, however, be easily achieved by glc as described below.

Glc of some triterpenes : The instrument used was a Pye Unicam, model GCD gas chromatograph equiped with columns (1.8 m×3 mm i.d.) containing 3% and 6% SE-30 ; carrier gas N_2 at 60 ml min^{-1} ; column temp. 260° and 312° ; detection and injection temp. 300° and 350°, respectively).

** St. Columbus College, Hazaribagh.

Derivatisation : About 1 mg each of the samples were dissolved in 10 μl of dried and distilled pyridine and to each 10 μl of *N,O*-bis(trimethylsilyl) acetamide[a] (Pierce Chemical, U.S.A.) was added and kept at 80° for 15 min. The sample (1-2 μl) was injected into the gas chromatograph. The retention time of the various compounds have been given in Table 1.

TABLE 1

Compounds	Retention times (minutes)
α-Amyrin	8.4
Lupeol	9.6
Betulin	18.6
Methyl betulinate	11.6
Methyl oleanolate	12.4
Methyl ursolate	18.2

Acetyl derivatives of the methyl esters of oleanolic, betulinic and ursolic acids were also gas chromatographed on the same column. The retention times were found longer than those of the trimethylsilyl ethers. Moreover, there were considerable trailing of the peaks and no separation was observed in the case of betulinic and oleanolic acids.

Acknowledgement

The authors are grateful to Prof. S. C. Bhattacharyya, Director, Bose Institute for his interest in the work and to R.S.I.C., Bose Institute for spectral analyses.

References

1. A. K. BARUA, S. P. DUTTA and S. K. PAL, *J. Chromatogr.*, 1967, **31**, 569.
2. G. R. WALLER, "Biochemical Application of Mass Spectrometry", Wiley-Interscience, New York, 1972, p. 375.
3. J. F. KLEBE, H. FINKBEINER and D. M. WHITE, *J. Am. Chem. Soc.*, 1966, **88**, 3390.

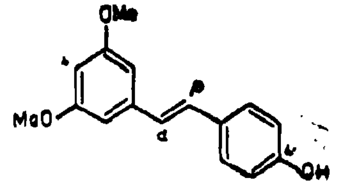
Chemical Examination of *Pterocarpus marsupium*

JAMES MATHEW and A. V. SUBBA RAO

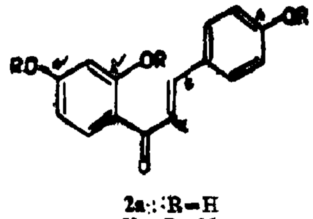
Department of Chemistry, Osmania University, Hyderabad-500 007

Manuscript received 6 February 1984, accepted 3 May 1984

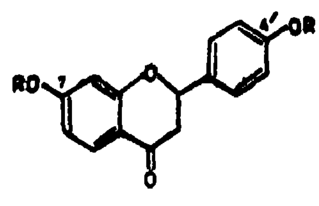
The powdered heartwood of *Pterocarpus marsupium* was successively extracted with petroleum ether (b.p. 60-80°) and chloroform. The petroleum ether extract on chromatography (Si-gel, eluent chloroform) yielded a colourless compound (0.01%), m.p. 294°, [α]D +74° (c 0.95 in $CHCl_3$) which was characterised as oleanolic acid {lit.[1] m.p. 310°, [α]D +78° ($CHCl_3$)} the identity of which was confirmed with mixed m.p. and superimposable ir spectrum with an authentic sample. This is the first instance of oleanolic acid from a *Pterocarpus* species, eventhough closely related acetyloleanolic acid has been found[a] to be present in these woods.



1



2a : R=H
2b : R=Me
2c : R=Ac



3a : R=H
3b : R=Me
3c : R=Ac

The petroleum ether extract also yielded pterostilbene (**1**) which we have reported[3] earlier. The ^{13}C nmr spectrum of pterostilbene (**1**) has now been recorded ; that of stilbenes appears to be scanty as reported in literature. The ^{13}C {^{1}H} nmr spectrum (90 MHz ; DMSO-d_6) of compound **1** showed 10 signals corresponding to the 16 carbon atoms of its molecular formula. The multiplicities in the off-resonance spectrum were in agreement with the assignments. The spectrum showed signals at δ 128.28 (s, C-1'), 127.65 (d, C-2', 6'), 115.30 (d, C-3', 5') and 160.38 (s, C-4') assignable to the carbon atoms of the ring B, approximately comparable to the signals due to the corresponding carbons of *p*-cresol[4] ; δ 157.13 (s, C-3, 5), 103.81 (d, C-2, 6), 98.99 (d, C-4) (the lone carbon appearing upfield by virtue of its *ortho*-relation to two oxygen functions on the aromatic rings) and 54.83 (OMe). Only one signal at δ 124.89 (d) was available to be assigned to both C-α and C-β. A signal at δ 139.35 (s) was tentatively assigned to C-1.

The chloroform extract on chromatography (Si-gel, eluent : chloroform-ethylacetate) gave compounds **2a** and **3a**. Compound **2a** (0.012%), yellow prisms, crystallised from ethylacetate-chloroform, m.p. 200° ; $C_{15}H_{12}O_4$, $M^{+\cdot}$ 256 ; ν_{max} (KBr) 1640 cm^{-1} (chelated CO) ; λ_{max} (MeOH) (log ε) 245 (3.96), 325 sh, 370 nm (4.45) ; was identified as 4,2',4'-trihydroxychalcone as its m.p.[5] and uv data[6] agreed with those reported. In the ^{1}H nmr spectrum of the compound **2a**, the signals due to the

protons of the carbon skeleton were comparable to that reported[7] in the case of 4,2'-dihydroxy-4'-methoxychalcone. Methylation and acetylation yielded the anticipated trimethyl ether[8] (**2b**) and triacetate[8] (**2c**), respectively; and their physical data agreed with those reported. The $^{13}C\{^1H\}$ nmr (90 MHz, DMSO-d_6) spectrum of compound **2a**, together with the off-resonance spectrum, showed signals at δ 191.26 (s, CO), 165.57 (s, C-2'), 164.81 (s, C-4'), 160.05 (s, C-4), 144.01 (d, C-β), 132.47 (d, C-6'), 130.90 (d, C-2, 6), 125.54 (s, C-1'), 117.14 (d, C-α), 115.67 (d, C-3, 5), 112.81 (s, C-1'), 107.98 (d, C-5) and 102.45 (d, C-3'); comparable to the signals due to the skeletal carbon atoms of the model compound 2'-hydroxy-4,4'-dimethoxychalcone[9]; nevertheless the anticipated[9] six-line multiplet of C-α and C-β in the off-resonance spectrum could be observed only as doublets.

Compound **3a** (0.009%); m.p. 207°, $[\alpha]_D - 26°$ (c 0.99 in MeOH); $C_{15}H_{12}O_4$, $M^{+\cdot}$ 256; ν_{max} (KBr) 1650 cm^{-1} (CO); λ_{max} (MeOH) (log ε) 240 sh, 280 (4.30), 314 nm (1.72), was characterised as 7,4'-dihydroxyflavanone (liquiritigenin) as the reported m.p.[10] and uv data[6] agreed with the observed, and it gave a deep violet colour in the Shinoda test[11]. The ^1H nmr spectrum of the compound **3a** was in agreement with the spectrum reported[7] for liquiritigenin. Methylation and acetylation of compound **3a** resulted in the anticipated dimethyl ether (**3b**)[12], and diacetate (**3c**)[10], respectively. In the $^{13}C\{^1H\}$ nmr (90 MHz, DMSO-d_6) spectrum of the compound **3a**, the signals due to the skeletal carbon atoms were comparable to that reported[9] for 7,4'-dimethoxyflavanone. The off-resonance spectrum showed multiplicities supporting the assignments. The pectrum showed signals at δ 189.85 (s, CO), 164.33 (s, C-7), 162.86 (s, C-8a), 157.28 (s, C-4'), 129.06 (s, C-1'), 128.14 (d, C-5), 127.98 (d, C-2', 6'), 114.86 (s, C-4a), 113.29 (d, C-3', 5'), 110.20 (d, C-6), 102.29 (d, C-8), 78.72 (d, C-2), and 42.91 (t, C-3).

It is notable that optically active liquiritigenin has been isolated in the present investigation. Earlier workers[13] who employed the method of alkali extraction and subsequent acidification for the isolation of this compound from several *Pterocarpus* woods, appears to have obtained a racemic form of it.

Acknowledgement

We wish to express our thanks to Prof. C. V. Ratnam and Prof. G. Srimannarayana, Department of Chemistry, Osmania University for helpful discussions.

References

1. H. R. Barton in "The Chemistry of Carbon Compounds", 1958, Vol. 2, Part B, p. 728.
2. N. Kumar, B. Ravindranath and T. R. Seshadri, *Phytochemistry*, 1974, **13**, 633.
3. J. Mathew, A. V. Subba Rao and N. V. Subba Rao, *Curr. Sci.*, 1977, **20**, 887.
4. E. Breitmair and W. Voelter, "¹³C NMR Spectroscopy", Verlag Chemie, 1974, p. 171.
5. R. G. Cooke and I. D. Rae, *Aust. J. Chem.*, 1964, **17**, 379.
6. L. Jurd in "The Chemistry of Flavonoid Compounds", ed. T. A. Geissman, Pergamon Press, New York, 1962, p. 107.
7. T. J. Mabry, K. R. Markham and M. B. Thomas, "The Systematic Identification of Flavonoids", Springer-Verlag, Berlin, 1970, p. 253.
8. B. Puri and T. R. Seshadri, *J. Sci. Ind. Res.*, *Sect. B*, 1954, **13**, 475.
9. A. Pelter, R. S. Ward and T. I. Gray, *J. Chem. Soc.*, *Perkin Trans. I*, 1976, 2475.
10. J. Shinoda and S. Ueeda, *Chem. Ber.*, 1934, **67**, 434.
11. J. Shinoda, *J. Pharm. Soc. Jpn.*, 1928, **48**, 214.
12. K. Juppen and S. V. Konstanecki, *Chem. Ber.*, 1904, **37**, 4161.
13. P. L. Sawhney and T. R. Seshadri, *J. Sci. Ind. Res.*, *Sect. C*, 1956, **15**, 154.

Sterols of *Salsola foetida*†

C. K. ANDHIWAL and KAMAL KISHORE*

Research Laboratory, Chemistry Department, S. V. College, Aligarh-202 001

Manuscript received 13 February 1984, revised 2 May 1984, accepted 30 May 1984

In the Ayurvedic system of medicine *Salsola foetida* (Chenopodiaceae) is highly used as vermifuge and the ashes of the plant are applied to itches[1]. Some alkaloids have earlier been detected in *Salsola* species[2], but no report was found on their phytosterol composition. The chemical examination of the light petroleum extract of *S. foetida* has now resulted in the isolation of five sterols.

Experimental

Air-dried and powdered plant material (820 g) was extracted thrice with light petroleum for 36 h under reflux. After the usual work up light petroleum extract gave 5.32 g neutral extract, which after purification was subjected to column chromatographic separation over silica gel (~25 fold excess). Elution with light petroleum ether: benzene (1 : 1) gave a sterol fraction which exhibited positive Liberman-Burchard test and gave yellow colour with tetranitromethane. Its ir spectrum (KBr) revealed the presence of OH (1040, 3400 cm^{-1}) and C=C (1610 cm^{-1}) groups. It was crystallised from methanol and gave shining flakes, m.p. 130-32° (tlc-homogeneous, silica gel – 5% $AgNO_3$, using several solvent systems). Since it was not found to be identical (m.m.p., co-tlc) with the available authentic specimen of sterols it was supposed to be a mixture which could not be separated further even by repeated column chromatography. For final confirmation the sterol fraction was then acetylated (Ac_2O-pyridine) and identification of each component was

† Presented in 20th Annual Convention of Chemists held at Cuttack, December, 1983.

carried out by comparison with authentic steryl acetate of the R_f on argentation tlc and relative retention time on glc.

Glc was performed on OV-17 on SCOT glass capillary column (30 m×0.3 mm i.d.) at 255°, injection at 275° and nitrogen carrier gas at 0.60 ml/min (split ratio *ca.* 100 : 1). RRT in glc was given relative to cholesteryl acetate. The other techniques used in the present work have been described previously[8]. The steryl acetates were shown to contain five phytosterols. The approximate content of each sterol in the acetylated total sterol fraction as determined by glc was : 24β-methylcholesta-5,22-dien-3β-ol acetate (brassicasterol, 12.3%) ; (24ξ)-24-methycholest-5-en-3β-ol acetate (campesterol, 5.2%) ; (22E, 24ξ)-24-ethylcholesta-5,22-dien-3β-ol acetate (stigmasterol, 36.9%) ; (24ξ)-24-ethylcholest-5-en-3β-ol acetate (β-sitosterol, 29.9%) ; and 24-ethylcholest-5,24-dien-3β-ol (15.7%) of RRT 1.96.

Discussion

It is known that three phytosterols (β-sitosterol, campesterol and stigmasterol) form the major components of sterols in many plants[4-6]. The number of sterols found in *Salsola foetida* is five, which include relatively large amounts of 24-ethylcholesta-5,24-dienol (15.7% of the total sterol) and brassicasterol (12.3%). The former sterol was first identified in *Withania somnifera*[6] and the later in *Solanaceous* seeds[7]. It was recently reported[8] to form biosynthetic intermediate for $\Delta^{24(28)}$-sterol to 24-alkylated sterol conversion.

Acknowledgement

The authors are grateful to Dr. S. C. Gupta, Principal and Dr. M. Behari, Head of the Chemistry Department, S. V. College, Aligarh for providing facilities. Sincere thanks are due to T. Matsumoto, Nihon University, Japan for glc analysis. Thanks are also due to U.G.C., New Delhi for the award of Junior Research Fellowship (K.K.).

References

1. R. N. CHOPRA, S. L. NAYAR and I. C CHOPRA, "Glossary of Indian Medicinal Plants", C.S.I.R., New Delhi, 1956, p. 219.
2. V. S. SOKOLOV, *Chem., Geol. U. Biol.*, 1956, **7**, 18.
3. C. K. ANDHIWAL, K. KISHORE, T. ITOH and T. MATSUMOTO, *J. Nat. Prod.*, 1982, **45**, 222.
4. M. BEHARI and C. K. ANDHIWAL, *Indian J. Chem., Sect. B*, 1977, **15**, 765.
5. C. K. ANDHIWAL, K. KISHORE and J. A. BALLENTINE, *J. Indian Chem. Soc.*, 1980, **57**, 1044.
6. W. J. S. LOCKLEY, D. P. ROBERT, H. H. REES and T. W. GOODWIN, *Tetrahedron Lett.*, 1974, 3773.
7. T. ITOH, T. TAMURA and T. MATSUMOTO, *Steroids*, 1977, **30**, 425.
8. M. L. MCKEAN and W. R. NEES, *Phytochemistry*, 1977, **16**, 683.

Chemical Investigation of *Lonicera maacki*

SARWAT SULTANA, MOHAMMED KAMIL and M. ILYAS*

Department of Chemistry, Aligarh Muslim University, Aligarh-202 001

Manuscript received 18 April 1983, revised 19 March 1984, accepted 26 May 1984

THE present investigation on the leaves of *Lonicera maacki* (Caprifoliaceae) resulted in the isolation and characterisation of three known compounds. In addition, the presence of three more biflavones have been indicated by tlc examination of methylated products.

Air dried and powdered leaves (1 kg) of *Lonicera maacki* was soxhleted with petroleum ether, benzene and chloroform successively for 3 h each. The residue after treatment with petroleum ether and benzene was chromatographed over silica gel using benzene : pyridine : formic acid (36 : 9 : 5) as solvent[1] for separation. Tlc revealed the presence of six bands.

The first compound (80 mg), R_f 0.18, m.p. 322°, was characterised as I-4', II-4', I-5, II-5, I-7, II-7 hexahydroxy (I-3', II-8) biflavone (amentoflavone). On methylation with dimethyl sulphate and anhydrous potassium carbonate in dry acetone it gave colourless crystals of hexa-*O*-methyl amentoflavone, m.p. 181-82°, ($CHCl_3$ – MeOH) R_f 0.40. Acetylation (Ac_2O/pyridine) of the compound yielded amentoflavone hexaacetate and crystallisation from $CHCl_3$ – MeOH gave colourless needless, m.p. 242-43°. The identity was confirmed by the comparison of ^{1}H-nmr spectra of the derivatives (methylether and acetate) with those of the authentic samples[2].

The second compound, m.p. 349° (MeOH) was identified as 5,7,4'-trihydroxy flavone and on methylation with dimethyl sulphate gave a trimethyl ether, m.p. 155°. It was characterised as apigenin by chromatographic and spectral comparision with an authentic sample[3].

The third flavanone, m.p. 228° gave an intense pink colour with Zn/HCl. Its identify with naringenin was established by direct comparison of the acetate and methyl ether with those of the authentic sample[4].

Tlc examination of the methylated product of the other three bands showed them to be identical with amentoflavone hexamethyl ether both in R_f value and colour. Tlc of the parent compounds indicated them to be mono-, di- and tri-*O*-methyl amentoflavone.

References

1. K. K. CHEXAL, B. K. HANDA and W. RAHMAN, *J. Chromatogr.*, 1970, **48**, 484.
2. M. KAMIL, M. ILYAS and W. RAHMAN, *Phytochemistry*, 1974, **13**, 2619.
3. N. A. KHAN, M. KAMIL and M. ILYAS, *Indian J. Chem., Sect. B*, 1979, **17**, 586.
4. W. RAHMAN and S. P. BHATNAGAR, *Aust. J. Chem.*, 1968, **21**, 539.

Titrimetric Determination of Manganese(II), Cobalt(II) and Nickel(II) with 1,2-Diaminocyclohexanetetraacetic Acid

RAM PARKASH,* SATWINDER KUMAR GUPTA,
R. P. SINGH and R. L. SINGHAL
Department of Chemistry, Panjab University, Chandigarh-160 014

Manuscript received 4 June 1983, accepted 3 May 1984

1,2-Diaminocyclohexanetetraacetic acid (DCTA) has been used previously for the determination of iron(III)[1,2], vanadium(IV)[3] and thorium(IV)[4]. In the present communication, its use has been extended to the visual and/or spectrophotometric determination of manganese(II), cobalt(II) and nickel(II).

Experimental

Reagents : DCTA (Koch-Light), manganese(II) sulphate tetrahydrate, cobalt(II) sulphate heptahydrate (BDH, AnalaR), nickel(II) sulphate hexahydrate, succinimide (E. Merck), thymolphthalexone (Koch-Light), catechol violet (BDH) and pyrogallol red (SD'S) were used as such. All other chemicals used were of guaranteed purity. Double distilled water was used throughout.

Solutions : The solutions of DCTA (0.005-0.05 *M*), manganese(II) sulphate, cobalt(II) sulphate, nickel(II) sulphate (5×10^{-2} *M*) and manganese ore (0.2 g/100 ml) were prepared and standardized or the manganese content estimated by the reported methods[5-7].

Apparatus : The *p*H of the solutions was measured with an ELICO model LI-10 *p*H meter. The spectrophotometric titrations were carried out using Specord UV VIS spectrophotometer and Beckman DU spectrophotometer using 1 cm cellls.

Visual determination of manganese(II) : The solutions of ascorbic acid (~1 ml, 0.1%), tartaric acid (~1 ml, 0.1%), thymolphthalexone indicator (10 drops, 0.05%) and sodium carbonate-hydrochloric acid buffer (~3 ml) of *p*H 9.75-10.50 were added to an aliquot (0.5-10 ml) of manganese(II) sulphate solution. The content were titrated with standard DCTA solution to a colour change from blue to almost colourless.

An aliquot (0.5-10 ml) of manganese(II) sulphate solution and solutions of triethanolamine (~1 ml, 8%), hydroxylamine hydrochloride (~1 ml, 2%) and catechol violet indicator (1 drop, 0.1%) were titrated with standard DCTA solution in the *p*H range 9.75-10.50 to a colour change from bluish green to violet. The *p*H was adjusted with ammonia-ammonium chloride buffer (~3 ml) of required *p*H.

Visual determination of cobalt(II) : An aliquot (0.5-5 ml) of cobalt(II) sulphate solution containing 10% succinimide solution (~5 ml) or pyrogallol red (10 drops of saturated solution in 50% ethanol) indicator was titrated with standard DCTA solution after adding ammonia-ammonium chloride buffer (2-5 ml) of *p*H 9.5-11.0 and 9.75-10.5 to a sharp colour change from blue to colourless and from blue to red, respectively.

Visual determination of nickel(II) : An aliquot (0.5-5 ml) of nickel(II) sulphate solution containing solutions of pyrogallol red (10 drops) and ascorbic acid (~5 ml, 0.1%) was titrated with standard DCTA solution after adding ammonia-ammonium chloride buffer (~5 ml) of *p*H 10.0-10.1 to a sharp colour change from blue to violet.

An aliquot of manganese(II), cobalt(II) or nickel(II) sulphate solution containing calcium(II), strontium(II) or barium(II) ions (2 ml, 5×10^{-2} *M*) was treated with potassium fluoride solution (3-5 ml, 1.2%) to mask these ions and the content was titrated against standard DCTA solution after buffering to proper *p*H. The interference due to copper(II) was dealt with by adding required amount of thiosulphate solution to an aliquot of these ions containing copper(II) solution. Lead(II) was removed by filtering off the precipitate of lead(II) sulphate formed by adding sulphuric acid (~1 ml, 0.5 *M*). The interference of mercury(II) (2 ml, 5×10^{-2} *M*) was dealt with by adding potassium iodide solution (~4 ml, 1%) before adding the buffer.

In the determination of manganese(II), the masking of silver(I), zinc(II), cadmium(II), cobalt(II) and nickel(II) ions (1 ml, 5×10^{-2} *M*) was carried out by adding potassium cyanide solution (3-4 ml, 1%) and hydroxylamine hydrochloride solution (~1 ml, 2%) to a solution of manganese(II) sulphate containing any of the above five metal ions. Iron(III) was removed by adding zinc oxide suspension to an aliquot of manganese(II) sulphate solution containing iron(III) ions. The iron(III) hydroxide so precipitated was filtered off and the resulting filtrate titrated as above after masking zinc(II) ions with potassium cyanide solution. An aliquot (5-10 ml) of manganese ore solution was titrated with DCTA according to the above procedure after the removal of iron(III) with zinc oxide suspension.

Spectrophotometric determination of manganese(II) and cobalt(II) : An aliquot (1-2 ml) of cobalt(II) solution and succinimide (~0.5 g), or that of manganese(II) solution (1-5 ml), triethanolamine (~1 ml, 8% solution), hydroxylamine hydrochloride solution (~1 ml, 2%) and thymolphthalexone (10 drops) or catechol violet (1 drop) indicator was titrated with standard DCTA solution in the *p*H range 9.75-10.50 at 590, 625 or 680 nm, respectively (Fig. 1). The absorbance was measured after each small addition of DCTA solution, corrected for dilution and then plotted as a function of the volume of DCTA added. The equivalence point was obtained by extrapolating the straight lines (Fig. 2).

These titrations were repeated at least five times at each concentration level with and without adding foreign ions.

Results and Discussion

A perusal of the results presented in Tables 1-5 suggests that DCTA reacts with manganese(II), cobalt(II) or nickel(II) in 1 : 1 molar ratio under the experimental conditions. The colour change at the end point in all these titrations is quite sharp indicating that there is no stepwise formation of successive complexes. The titration procedure is simple and consumes very little time. As little as 0.14, 0.13 and 0.13 mg of manganese(II), cobalt(II) and nickel(II), respectively can be quantitatively determined.

The blue, bluish green and blue complexes formed by manganese(II) with thymolphthalexone or catechol violet and by cobalt(II) with succinimide in the pH range 9.75-10.50 have maximum absorbance at ~625, 680 or 590 nm, respectively (Fig 1). The corresponding DCTA-metal complexes do not show significant absorbance at these wave lengths. Since the DCTA-metal complex is stronger than metal-indicator complex under the experimental conditions, the colour of the latter disappears gradually as the equivalence point is approached in the titration of metal-indicator solution with DCTA. After the equivalence point, the absorbance remains almost constant (Fig. 2). The standard deviation in spectrophotometric titration is less than that in the visual method.

The spectrophotometric titration of nickel(II) is not carried out due to non-availability of a suitable indicator.

Interferences : Interfering effect of the metal ions depends primarily on the difference in conditional stability constants of the various metal ions present in the solution. In the present study, it is observed that manganese(II), cobalt(II) or nickel(II)

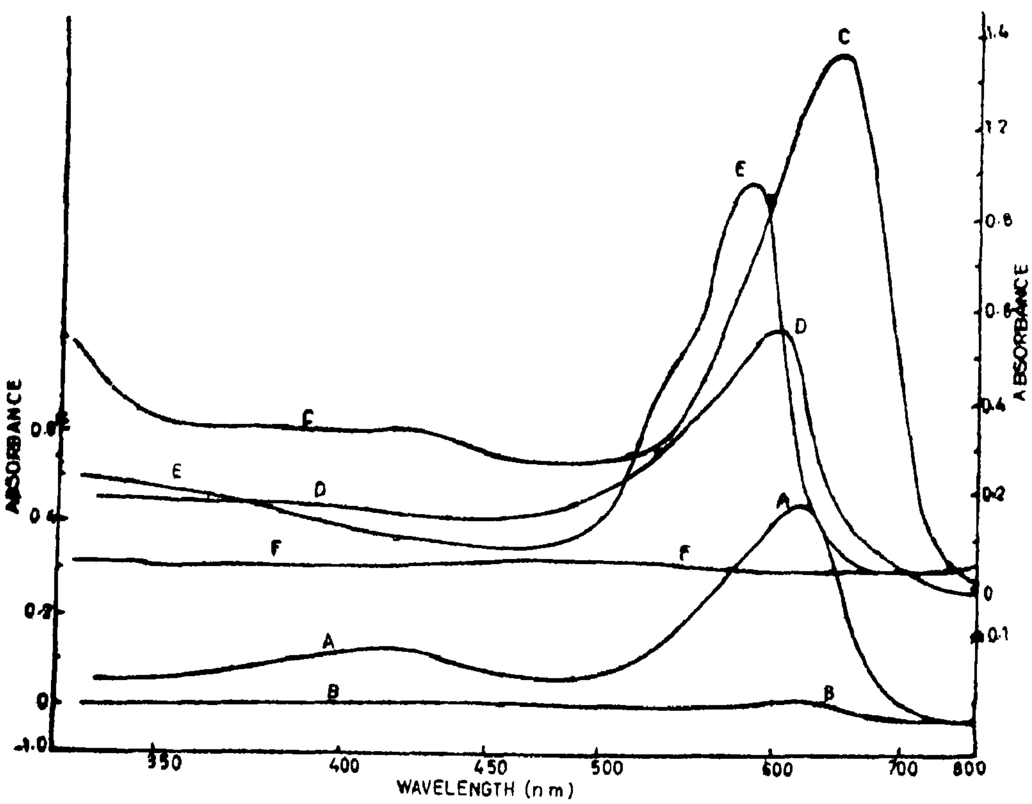


Fig. 1. Absorption spectra of metal ion – indicator complexes and DCTA-metal ion complexes.

A : 1.43×10^{-3} *M* Manganese(II), 8% Triethanolamine, 2% Hydroxylamine hydrochloride, 0.05% Thymolphthalexone indicator, pH 10.00, 1.32×10^{-3} *M* DCTA.

B : 1.48×10^{-3} *M* Manganese(II), 8% Triethanolamine, 2% Hydroxylamine hydrochloride, 0.05% Thymolphthalexone, pH 10.00, 1.32×10^{-3} *M* DCTA.

C : 1.43×10^{-3} *M* Manganese(II), 8% Triethanolamine, 2% Hydroxylamine hydrochloride, 0.1% Catechol violet, pH 10.00.

D : 1.43×10^{-3} *M* Manganese(II), 8% Triethanolamine, 2% Hydroxylamine hydrochloride, 0.1% Catechol violet, pH 10.00, 1.32×10^{-3} *M* DCTA.

E : 2.50×10^{-3} *M* Cobalt(II), 0.5 g Succinimide indicator, pH 10.6.

F : 2.50×10^{-3} *M* Cobalt(II), 0.5 g Succinimide indicator, 1.77×10^{-3} *M* DCTA, pH 10.6 ; Path length 1 cm.

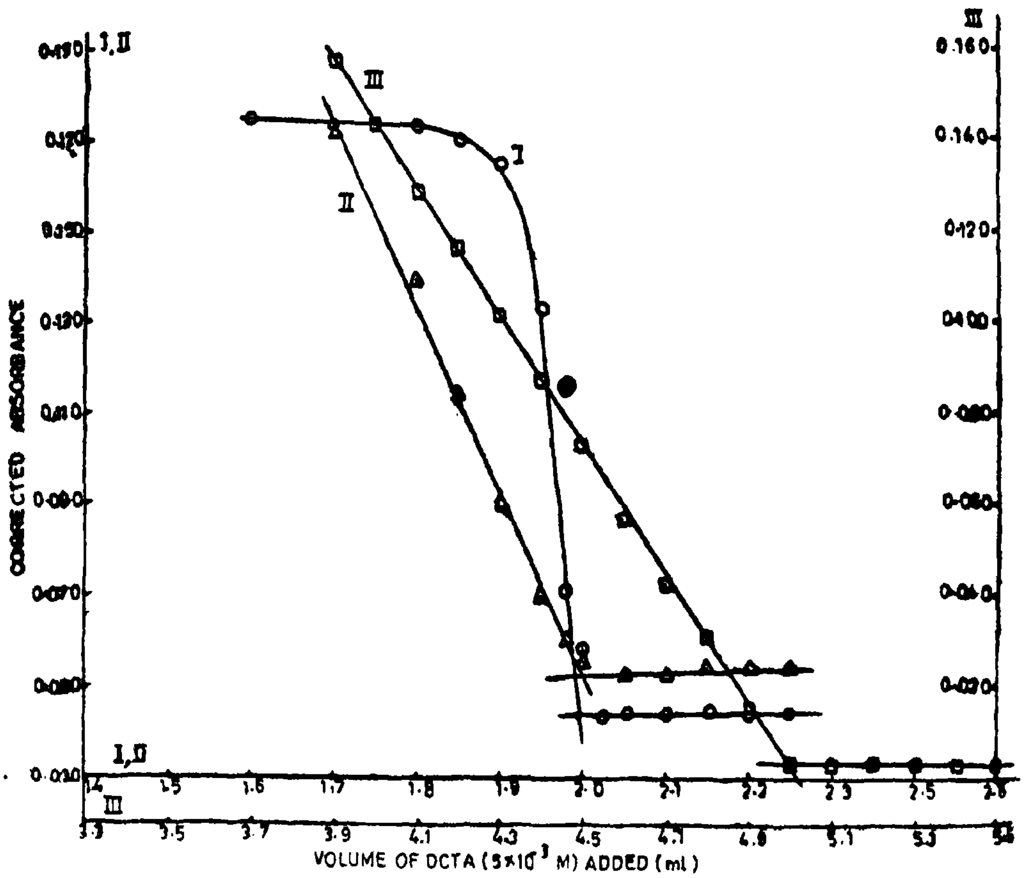


Fig. 2. Spectrophotometric titrations of metal ions with DCTA using metal chromic indicators.

Curve I and II : Titrations of manganese(II) (2.00 ml, 5×10^{-3} M) with DCTA using thymolphthalexone indicator at 625 nm (○—○) and catechol violet indicator at 680 nm (△--△).

III : Titration of cobalt(II) (5.00 ml, 5×10^{-3} M) with DCTA using succinimide indicator at 590 nm (⊡—⊡).

TABLE 1—VISUAL DETERMINATION OF MANGANESE(II) WITH DCTA IN PRESENCE OF VARIOUS IONS USING THYMOLPHTHALEXONE AND CATECHOL VIOLET INDICATORS

Ion added mg	Amount of manganese(II) mg			Standard deviation $\times10^{2}$	
	Taken	Found using			
		Thymolphthalexone	Catechol violet	Thymolphthalexone	Catechol violet
	0.14	0.14	0.14	1.0	1.1
	1.87	1.87	1.87	1.0	0.9
	2.75	2.74	2.75	1.2	1.0
Ag^{+}					
1.86	0.69	0.68*	0.69*	1.2	1.3
17.57	1.79	1.80*	1.81*	0.9	1.4
45.95	2.34	2.33*	2.35*	1.0	1.1
Zn^{2+}					
0.65	0.55	0.55*	0.54*	1.0	1.2
8.15	1.37	1.38*	1.38*	1.1	1.3
26.18	2.20	2.19*	2.20*	1.2	1.0
Cd^{2+}					
0.84	0.41	0.41*	0.41*	1.4	1.3
19.64	1.92	1.90*	1.91*	1.2	1.1
50.58	2.47	2.46*	2.47*	1.2	1.2
Ca^{2+}					
0.40	0.55	0.55*	0.55*	1.2	1.3
4.99	1.87	1.86*	1.88*	0.9	1.4
16.05	2.20	2.18*	2.19*	1.0	1.1
Sr^{2+}					
0.65	0.41	0.41*	0.41	1.0	0.9
13.16	1.65	1.65*	1.65*	1.4	1.1
39.39	2.47	2.48*	2.49*	1.3	1.2
Ba^{2+}					
0.67	0.27	0.27*	0.27*	1.4	1.2
20.62	1.65	1.63*	1.63*	1.3	1.1
61.75	2.47	2.49*	2.46*	1.2	1.0
Cu^{2+}					
0.47	0.41	0.41*	0.41*	1.0	0.8
6.26	1.09	1.07*	1.08*	0.9	0.9
14.30	1.24	1.22*	1.22*	1.0	1.2
Hg^{2+}					
5.50	1.51	1.50*	1.52*	1.4	1.0
37.25	2.06	2.06*	2.08*	1.2	1.3
95.30	2.60	2.61*	2.62*	1.0	1.2
Pb^{2+}					
3.09	0.82	0.82*	0.82*	1.4	1.3
16.10	1.65	1.66*	1.67*	1.2	1.0
93.17	2.47	2.48*	2.49*	0.9	1.1
Fe^{3+}					
0.56	0.55	0.55*	0.54*	1.0	1.3
7.68	1.51	1.52*	1.52*	1.4	0.9
26.53	2.61	2.63*	2.63*	1.2	1.1

(Table 1 contd.)

* After masking/removing the interfering ions.

TABLE 2—VISUAL AND SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) WITH DCTA IN PRESENCE OF VARIOUS IONS USING SUCCINIMIDE INDICATOR

Ion added mg	Amount of cobalt(II) mg			Standard deviation $\times 10^2$	
	Taken	Found Visually	Found Spectrophotometrically	Visually	Spectrophotometrically
	0.15	0.15	0.15	1.2	0.2
	0.81	0.81	0.81	1.1	0.8
	1.47	1.46	1.47	1.2	0.4
Ag^{+}					
0.81	0.44	0.44	interferes	1.4	–
2.69	1.47	1.45	interferes	1.8	–
5.88	1.47	interferes	interferes	–	–
Ca^{2+}					
0.80	0.44	0.44*	interferes	1.4	–
2.51	0.74	0.73*	interferes	1.4	–
7.01	1.08	1.02*	interferes	1.3	–
Sr^{2+}					
0.88	0.59	0.59*	interferes	1.2	–
6.57	0.88	0.88*	interferes	1.1	–
21.91	1.47	1.46*	interferes	1.0	–
Ba^{2+}					
1.20	0.52	0.52	0.52	1.1	0.3
3.43	1.47	1.46	1.47	1.0	0.4
6.86	1.47	interferes	interferes	–	–
Cu^{2+}					
0.82	0.29	0.29*	interferes	1.2	–
4.75	0.88	0.88*	interferes	1.2	–
11.91	1.11	1.12*	interferes	1.8	–
Hg^{2+}					
1.25	0.37	0.37*	interferes	1.1	–
12.50	0.74	0.73*	interferes	1.4	–
40.20	1.18	1.18*	interferes	1.5	–
Pb^{2+}					
1.04	0.29	0.29*	interferes	1.2	–
2.59	0.74	0.74*	interferes	1.0	–
4.66	1.33	1.35*	interferes	1.3	–
La^{3+}					
1.04	0.44	0.44	0.44	1.2	0.3
3.47	1.47	1.45	1.46	1.3	0.4
6.94	1.47	interferes	interferes	–	–
S^{2-}					
0.20	0.37	0.37	0.37	1.4	0.5
0.80	1.47	1.48	1.47	1.3	0.4
1.60	1.47	interferes	interferes	–	–

* After masking/removing the interfering ions.

TABLE 3—VISUAL DETERMINATION OF COBALT(II) AND NICKEL(II) WITH DCTA IN PRESENCE OF VARIOUS IONS USING PYROGALLOL RED INDICATOR

Ion added mg	Amount taken mg		Amount found mg		Standard deviation $\times 10^2$	
	Co^{2+}	Ni^{2+}	Co^{2+}	Ni^{2+}	Co^{2+}	Ni^{2+}
	0.15	0.15	0.15	0.15	1.2	1.3
	0.88	0.78	0.87	0.78	0.8	1.2
	1.47	1 47	1.46	1.45	1.1	1.1
Ag^{+}						
1.21	0.66	0.66	0.66	0.66	1.2	1.2
2.69	1.47	1.47	1.45	1.45	1.3	1.3
5.88	1.47	1.47	interferes	interferes	–	–
Ca^{2+}						
0.20	0.29	0.44	0.28*	0.45*	1.0	1.2
1.50	0.44	0.81	0.43*	0.82*	0 9	1.3
4.01	0.59	1.25	0.58*	1.26*	1.4	1.4
Sr^{2+}						
1.09	0.74	0.51	0.73*	0.51*	1.2	1.1
8.76	1.18	0.66	1.18*	0.66*	0.9	1.4
19.71	1.33	1.10	1.32*	1.11*	1.3	1.3
Ba^{2+}						
1.20	0.52	0.29	0.52	0.29	1.2	1.1
3.43	1.47	1.47	1.46	1.45	1.1	1.2
6.86	1.47	1.47	interferes	interferes	–	–
Cu^{2+}						
0.40	0.37	0.15	0.37*	0.15*	1.1	1.2
0.87	0.81	0.88	0.82*	0.88*	1.0	1.1
11.92	1.11	1.08	1.10*	1.04*	1.1	1.4
Hg^{2+}						
1.25	0.37	0.44	0.37*	0.44*	1.1	1.1
11.28	0.66	1.17	0.66*	1.18*	1.0	1.2
32.60	0.96	1.32	0.97*	1.33*	1.1	1.4
Pb^{2+}						
4.14	1.18	0.37	1.19*	0.37*	1.3	1.2
4.40	1.25	0.73	1.24*	0.72*	1.5	1.4
4.92	1.40	1.39	1.42*	1.41*	1.4	1.5
S^{2-}						
0.20	0.37	0.15	0.36	0.15	1.1	1.4
0.80	1.47	1.47	1.46	1.49	1.4	1.3
1.60	1.47	1.47	interferes	interferes	–	–
PO_4^{3-}						
3.60	0.22	0.59	0.22	0.59	1.3	1.1
47.88	1.47	0.88	1.46	0.88	1.2	1.1
236.89	1.47	1.32	interferes	1.33	–	1.3

* After masking/removing the interfering ions.

TABLE 4—VISUAL DETERMINATION OF A BINARY MIXTURE OF MANGANESE(II) AND COBALT(II) WITH DCTA USING THYMOLPHTHALEXONE AND CATECHOL VIOLET INDICATORS

Indicator	Amount taken, mg		Amount found, mg		Standard deviation $\times 10^2$	
	Mn^{2+}	Co^{2+}	Mn^{2+}	Co^{2+}*	Mn^{2+}	Co^{2+}
Thymol-phthalexone	0.82	0.59	0.83	0.59	1.4	1.2
	1.65	1.18	1.66	1.18	1.2	1.3
	2.47	2.47	2.44	2.50	1.1	1.1
Catechol violet	0.27	0.59	0.27	0.59	1.1	1.2
	1.65	0.88	1.64	0.88	1.2	1.0
	2.61	1.18	2.68	1.19	1.4	1.3

* From difference in titration values in presence and absence of the masking agent.

TABLE 5—VISUAL DETERMINATION OF A BINARY MIXTURE OF MANGANESE(II) AND NICKEL(II) WITH DCTA USING THYMOLPHTHALEXONE AND CATECHOL VIOLET INDICATORS

Indicator	Amount taken mg		Amount found mg		Standard deviation $\times 10^2$	
	Mn^{2+}	Ni^{2+}	Mn^{2+}	Ni^{2+}*	Mn^{2+}	Ni^{2+}
Thymol-phthalexone	0.55	0.29	0.55	0.28	1.1	1.3
	1.65	0.88	1.66	0.88	1.0	1.1
	2.75	1.18	2.78	1.19	1.2	1.0
Catechol violet	0.82	0.59	0.82	0.58	1.2	1.4
	1.87	0.88	1.86	0.88	1.0	0.8
	2.75	1.47	2.77	1.46	1.3	0.9

* From difference in titration values in presence and absence of the masking agent.

is determined quantitatively in presence of 100 times as much of lithium, sodium, potassium, fluoride, chloride, iodide, nitrate and sulphate ions. Equimolar amount of barium(II) ions is bearable in these titrations except when thymolphthalexone is used as indicator in the determination of manganese. Upto 100 times excess of phosphate does not interfere under the experimental conditions except in the determination of cobalt(II) employing pyrogallol red as indicator where only 20 times excess is bearable. Upto 100 times excess of thiosulphate does not interfere in these titrations except when succinimide is used as indicator in the estimation of cobalt(II) where even its traces interfere seriously. Equimolar amount of silver(I) ions is bearable in visual estimation of cobalt(II) or nickel(II) though a precipitate of silver hydroxide is formed. However, it interferes in the determination of manganese(II). Lanthanum(III) interferes except in titration using succinimide as indicator in the determination of cobalt(II) where even its equimolar amount causes no interference.

Magnesium(II), nickel(II) and cobalt(II) ions are co-titrated with manganese(II) quantitatively and thus interfere in these titrations. The amount of DCTA used is exactly the same as that required for the sum of any of these ions present and manganese(II). However, the titration is not possible in the presence of higher amounts of cobalt(II) and nickel(II) because the end point can not be detected accurately due to their intense colour. Calcium(II), strontium(II), copper(II), mercury(II), lead(II), zinc(II), aluminium(III), iron(III), chromium(III) and thorium(IV) interfere seriously in these titrations.

In visual titrations, calcium(II), strontium(II) and barium(II) ions are masked with potassium fluoride solution as their slightly soluble fluorides do not interfere. Copper(II) and mercury(II) are masked with thiosulphate and potassium iodide, respectively when non-interfering copper(II)-thiosulphate complex or $[HgI_4]^{2-}$ complex ion is formed. Lead(II) is precipitated out as its sulphate with 0.5 *M* sulphuric acid and removed by filtration.

In the estimation of manganese(II), the masking of silver(I), zinc(II), cadmium(II), cobalt(II) and nickel(II) is effected with aqueous potassium cyanide solution and hydroxylamine hydrochloride when the corresponding stable cyano-complexes of these ions are formed. Potassium cyanide does not form a complex with manganese(II) under the experimental conditions. Since hydroxylamine hydrochloride is already present in the titrations using catechol violet as indicator, addition of more of this reagent is not required. The method is thus utilized for the analysis of a binary mixture of manganese(II) with cobalt(II) or nickel(II). The interference due to iron(III) is removed by adding zinc oxide suspension and filtering off the precipitated iron(III) hydroxide. The excess zinc oxide is masked with potassium cyanide.

The method is of particular significance for the determination of manganese(II) in its ore. The method is simple and no vigorous shaking and heating (80-90°) are required unlike the conventional potassium permanganate titration method. Iron(III) is removed before estimating manganese(II) according to the procedure mentioned above. Other constituents of the manganese ore do not interfere in the titration. Manganese(II) is thus estimated in manganese ore with ± 0.55% error (Table 6).

TABLE 6—DETERMINATION OF MANGANESE(II) IN MANGANESE ORE WITH DCTA USING THYMOLPHTHALEXONE AND CATECHOL VIOLET INDICATORS

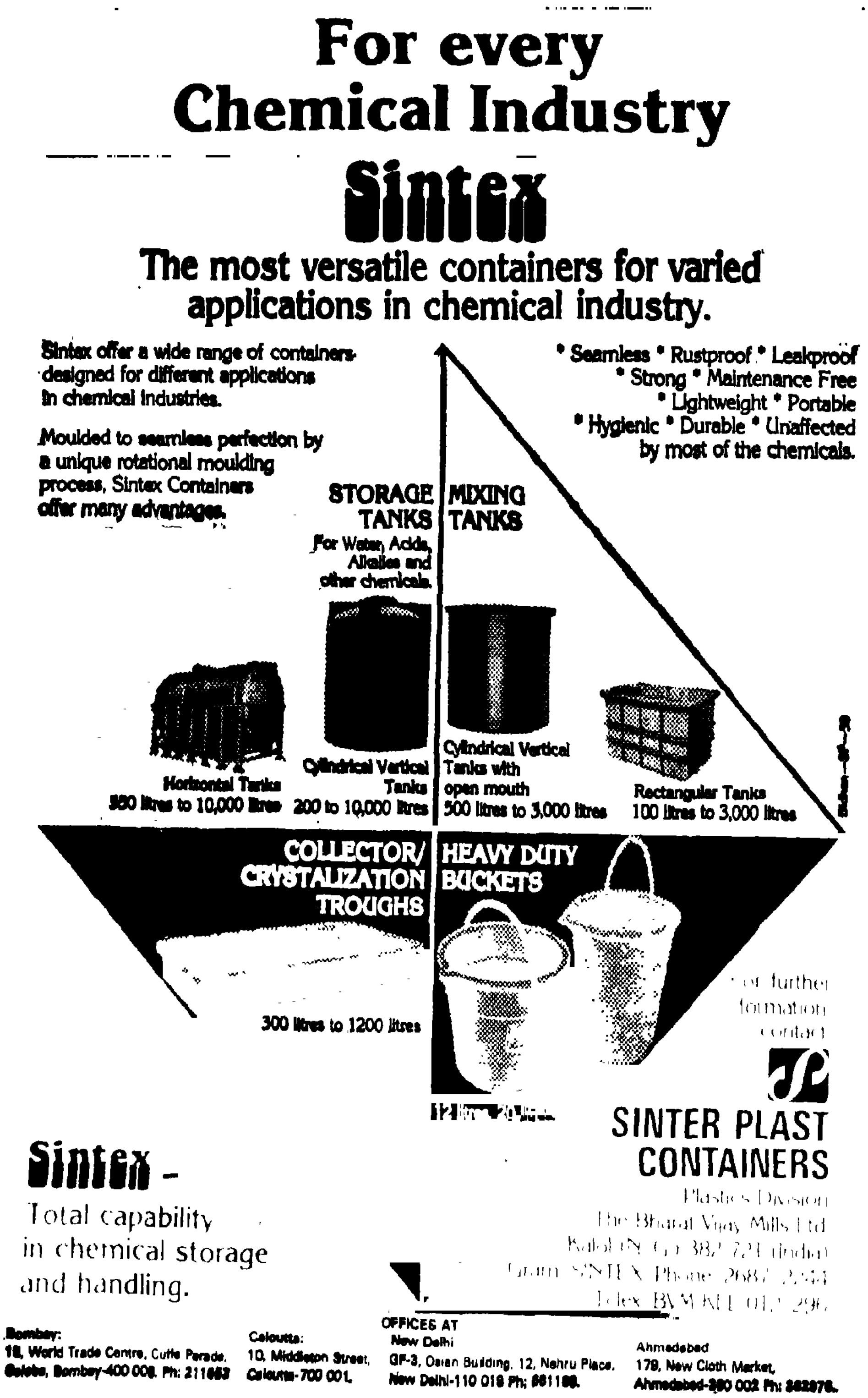
Manganese(II) found mg			% Error	
Reported method	Thymolphthalexone	Catechol violet	Thymolphthalexone	Catechol violet
392.97	390.79	390.81	−0.55	−0.55
390.22	391.42	391.98	+0.31	+0.45
389.06	390.88	390.52	+0.47	+0.38

An attempt to mask other interfering ions with common masking agents is not successful.

References

1. R. PARKASH, R. BALA and R. L. SINGHAL, *Talanta*, 1979, **26**, 575; *J. Indian Chem. Soc.*, 1979, **56**, 1188.
2. R. PARKASH and R. L. SINGHAL, *Acta Ciencia Indica*, 1982, **8**, 218.
3. R. PARKASH, S. K. REHANI and R. L. SINGHAL, *Curr. Sci.*, 1980, **49**, 269.
4. R. PARKASH, S. K. REHANI, S. K. SHARMA, A. DUTT and R. L. SINGHAL, *Res. Bull.* (*Science*) *P. U.*, 1982, **33**, 73.
5. R. PRIBIL, *Collect. Czech. Chem. Commun.*, 1955, **20**, 162.
6. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longmans Green, London, 1971, pp. 434, 435, 530.
7. "Manual of Procedures for Chemical and Instrumental Analysis of Ores, Minerals and Ore Dressing Products", Ministry of Steel and Mines, Nagpur, 1979, p. 111.

J. Indian Chem. Soc.,
Vol. LXI, August 1984.



J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 737-743

Chemical Applications of *X*-ray Spectroscopy*

A. SYAMAL

Department of Chemistry, Regional Engineering College, Kurukshetra-132 119

The study of the *X*-ray absorption or *X*-ray emission spectrum of an atom in a molecule leads to important informations on the nature of chemical bonding (bonding sites, bond distance, bonding character, degree of covalency), valence state, coordination symmetry, and electronic structure of an atom in a molecule. The relation between the *X*-ray spectra and various solid state phenomena, such as valence state, bond distance, bonding character, and coordination symmetry are discussed. A number of examples have been presented to illustrate the various possibilities of the *X*-ray spectroscopy of the bonded atoms.

N recent years there has been considerable research interest in the influence of chemical bonding on the *X*-ray spectrum since the analysis of the fine features of the *X*-ray spectrum of the bonded atom provides a wealth of information regarding the valence state, oxidation-reduction phenomena, coordination, bonding, bond distance, and electronic structure of the atom under study. The *X*-ray spectroscopy has the advantage in characterising thin films and very small amount of poorly crystalline, glassy and liquid samples, and refractory materials which are difficult to characterise by conventional techniques (*e.g.*, *X*-ray diffraction) or when the assignment of structure is not possible from magnetic measurements due to the inconclusive nature of the magnetic moment. The soft *X*-ray spectroscopy deals with the soft or low energy *X*-rays and is also known as low-energy *X*-ray spectroscopy. The basic principles of *X*-ray excitation for both the soft *X*-rays and more energetic or harder *X*-rays used in *X*-ray diffraction, are, however, the same.

In order to understand the origin of the *X*-ray spectrum of an atom let us consider the energy level diagram of aluminium presented in Fig. 1 in which the possible electron transitions have also been indicated. On absorption of *X*-rays, an electron is promoted from an inner level into an unoccupied level and the electron transitions from the K and $L_{2,3}$ levels to the valence electron levels lead to the *X*-ray K-absorption spectrum and the *X*-ray $L_{2,3}$ absorption spectrum, respectively. Since the valence electrons are involved in the formation of the chemical bonds, these *X*-ray absorption transitions are susceptible to significant changes when a change in chemical environment occurs. The *X*-ray absorption spectrum provides valuable information regarding the unoccupied part of the energy band system. On the other hand, the *X*-ray transitions occurring due to the electron transitions

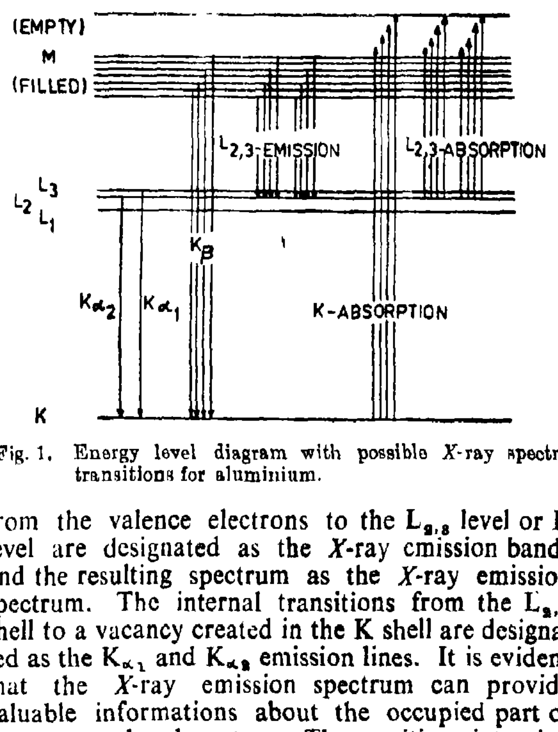


Fig. 1. Energy level diagram with possible *X*-ray spectral transitions for aluminium.

from the valence electrons to the $L_{2,3}$ level or K level are designated as the *X*-ray emission bands and the resulting spectrum as the *X*-ray emission spectrum. The internal transitions from the $L_{2,3}$ shell to a vacancy created in the K shell are designated as the K_{α_1} and K_{α_2} emission lines. It is evident that the *X*-ray emission spectrum can provide valuable informations about the occupied part of the energy band system. The position, intensity, width and fine structure of the *X*-ray absorption and the *X*-ray emission spectra are characteristics of the bonded atoms and provide much valuable informations about the electronic structure of the materials. The applications of *X*-ray K-absorption spectroscopy in chemical bonding form the major part of this article. The electronic transitions occurring in the *X*-ray absorption spectroscopy are governed by the selection rule : $\Delta l = \pm 1$, where l is the orbital angular momentum quantum number. Thus, the transitions $1s \rightarrow 4p$, $1s \rightarrow 5p$, $2p \rightarrow 4d$ and $2p \rightarrow 5d$ are allowed transitions. On the other hand, the transition $1s \rightarrow 3d$ is a forbidden transition

* Rev. Fr. L. M. Yedanapalli Memorial Lecture (1981) delivered under the auspices of the Indian Chemical Society on 8 September, 1984 at Gwalior.

($\Delta l = \pm 2$). But due to the mixing of the s or d character with the p character by various mechanisms in transition metal compounds, the above selection rule is relaxed to some extent and the transitions $1s \rightarrow 3d$ and $1s \rightarrow 4s$ may become partially allowed.

Other than the above *X*-ray transitions, weaker emission lines are observed immediately to the high energy side of the K_{α_1}, K_{α_2} lines. These are known as satellites which are due to the doubly ionised atoms. These satellites arise from the $L_{2,3} \rightarrow K$ transitions in presence of two simultaneous electron vacancies in the K and L shells. Although these satellites are quite weak in case of 3*d* transition metals, these lines are relatively intense in the elements of the third period of the Periodic Table and can be separated from the parent K_α line. Usually three satellites are observed and these are designated as $K_{\alpha'}$, K_{α_3} and K_{α_4} lines. The influence of chemical bonding is also observed in these satellite lines. The energy shifts of the satellite lines occur towards the higher energy as the oxidation state of the metal ion increases. The $K_{\alpha_4}/K_{\alpha_3}$ intensity ratio increases from the lower oxidation state to the higher oxidation state. The more covalent is the bond, the lower is the $K_{\alpha_4}/K_{\alpha_3}$ intensity ratio and the lower is the energy position of the K_{α_3} and K_{α_4} satellite lines[1-5].

In the *X*-ray K-absorption spectroscopy the following regions are of interest to the chemists.

(a) Low energy region (0-20 eV),

(b) Energies up to 40 eV higher than the energy of the main absorption edge (Kossel fine structure),

(c) Energies in the region 40-150 eV,

(d) Energies beyond 150 eV (Kronig fine structure).

Applications of X-*ray spectroscopy :*

Nature of chemical bond : The *X*-ray spectroscopy is useful not only to find out the presence of a particular element but it can also give indication of how the bonded atom is combined chemically. The *X*-ray spectrum of the bonded atom is also useful to find out the metal-ligand chromophore system (MO_5N, MO_2N_2, MN_2O_4, MO_4N_2 *etc*), metal-ligand bond distance, and degree of covalency. A typical *X*-ray K-absorption spectrum of a compound is presented in Fig. 2 in which the absorption coefficient is plotted against energy in electron volt. In Fig. 2 there is an absorption maximum of low intensity (denoted by 'a') appearing at the low energy side of the main absorption edge. 'A' and 'B' denote the absorption maxima and α, β denote the absorption minima. 'A' represents the principal absorption maximum. The 'edge width' is defined as the energy difference between the principal absorption maximum A and the first inflection point of the main absorption edge K (Fig. 3).

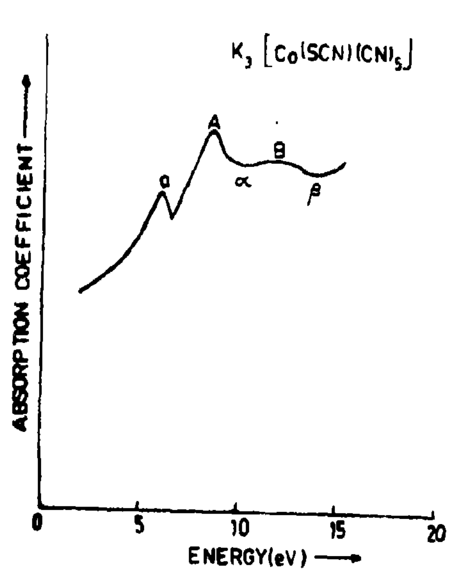


Fig. 2. *X*-Ray K-absorption spectrum[6] of $K_3[Co(SCN)_5(CN)_5]$

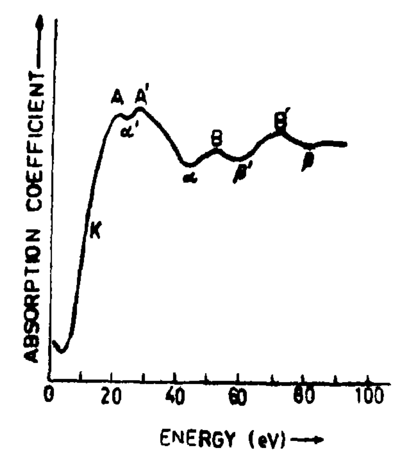


Fig. 3. *X*-Ray K-absorption spectrum of *N,N'*-tetramethylene-bis(salicylideneimine)cobalt(II).

The discipline of chemistry is one of the most beautifully balanced subjects with regard to the theory and experiment so that one can theoretically predict enough to make the subject interesting and yet there is sufficient scope for the experimental verification of the theoretical prediction. This is demonstrated below in few examples[6] from the *X*-ray K-absorption spectra of metal-thiocyanato and metal-isothiocyanato bonded coordination compounds*.

The ambident nature of the thiocyanate ion is well known. Both sulphur and nitrogen atoms may be bonded to the metal resulting in M – S or M – N linkage. The molecular orbital energy level diagram

* The use of the term "complex" in coordination chemistry is confusing and should not be used. The suitable names have been suggested for the terms associated with the word "complex" *e.g.*, coordination compound for complex compound, coordination titration for complexometric titration, *etc*[8].

of the thiocyanate ion[9] is presented in Fig. 4. It is evident from the MO diagram that the lowest un-

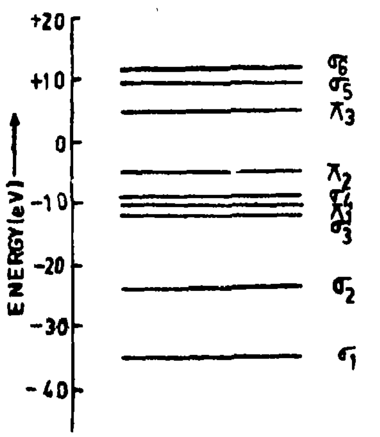


Fig. 4. Molecular orbital energy level diagram of thiocyanate ion[9].

filled level is π_3, a combination that is antibonding between the neighbouring atoms and is concentrated on the central atom. The highest filled level is π_2 which is a combination that is localised on the end atoms and is essentially non-bonding. In the coordination compounds of the thiocyanate ion the π_2 level is mainly localised on the sulphur atoms and the M – SCN bond is formed by the overlap of the metal orbitals with the π_2 orbital of thiocyanate ion. On the other hand, the M – NCS bond results from the overlap of the metal orbitals with the *sp* hybridized σ orbital of nitrogen. It is well known that *S*CN behaves as both π-donor and σ-donor but *N*CS acts as a σ-donor. In the thiocyanato-S coordination compounds the π_2 level acts as a π-donor and a vacancy is created in the π_2 level. On the absorption of *X*-rays, the ejected 1*s* electron would jump to the lowest energy empty π_2 level and this would lead to the observation of an *X*-ray K-absorption transition due to $1s \rightarrow \pi_2$ at low energy. But in the thiocyanato-N coordination compounds with M – NCS linkage, the π_2 level is primarily localised on the sulphur atom and the low energy $1s \rightarrow \pi_2$ transition is not expected to be observed. From the study of the *X*-ray K-absorption spectra of several thiocyanato coordination compounds, where the presence of M – SCN or M – NCS has been established firmly by other physico-chemical studies, we have shown that the above theoretical prediction is indeed correct[6]. In the *X*-ray K-absorption spectra of the thiocyanato-S coordination compounds K_2[Pt(SCN)$_6$], K_3[Co (SCN)(CN)$_5$], and *trans*-NH_4[Co(SCN)$_2$(DMGO)$_2$].3H_2O (where DMGO = monoanion of dimethylglyoxime), a low energy absorption maximum 'a' of medium intensity at around 7 eV (Figs. 5 and 6) appears and this indicates the presence of M – SCN bonding in these coordination compounds[6]. On the other hand, in the *X*-ray K-absorption spectra of the thiocyanato-N coordination compounds K_2[Co(NCS)$_4$].4H_2O, K_3[Co(NCS)(CN)$_5$], and [Fe(NCS)$_2$(py)$_4$] (where py =

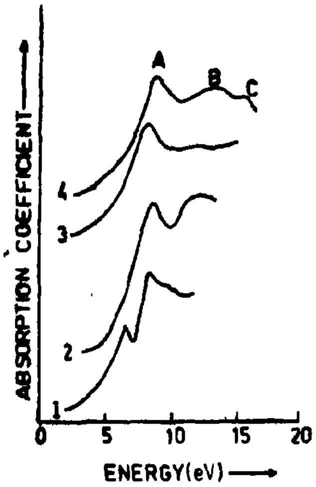


Fig. 5. *X*-Ray K-absorption spectrum[6] of (1) K_2[Pt(SCN)$_6$], (2) K_2[Co(NCS)$_4$].4H_2O, (3) K_3[Co(NCS)(CN)$_5$], and (4) KSCN.

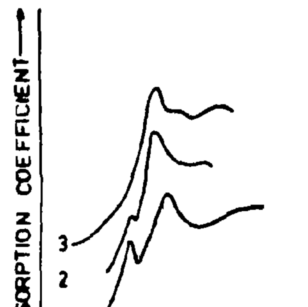


Fig. 6. *X*-Ray K-absorption spectrum[6] of (1) NH_4[Co-(SCN)$_2$(dimethylglyoxime)$_2$].3H_2O, (2) [Co(thiocyanate)(PPh$_3$)(dimethylglyoxime)$_2$], and (3) [Fe(NCS)$_2$(py)$_4$].

pyridine), no such low energy absorption maximum was observed[6] in accordance with the above prediction. In the *X*-ray K-absorption spectrum (curve 2, Fig. 6) of [Co (thiocyanate) (PPh$_3$) (DMGO)$_2$] which is a linkage isomeric mixture with the thiocyanato-S isomer being dominant, the intensity of the low energy absorption maximum is significantly lowered as both types of thiocyanato-S and thiocyanato-N isomers are present in the compound[6]. Thus, the *X*-ray K-absorption spectroscopy is also useful to identify the presence of the mixture of linkage isomers in a coordination compound. In Fig. 5 (curve 4) the *X*-ray K-absorption spectrum of ptoassium thiocyanate which contains ionic thiocyanate, has also been included. The low energy absorption maximum 'a' is absent in the *X*-ray K-absorption spectrum of KSCN and a small increase in the value of the absorption coefficient was noticed in this low energy region. This is in line with the fact that the π_2 level in the thiocyanate ion is approximately divided between the sulphur and nitrogen

ends in the thiocyanate ion. The energy separations between the maxima A – B = 5 eV, and B – C = 3 eV correspond to π_g-σ_g and σ_g-σ_g, respectively and are in accordance with the MO diagram depicted in Fig. 4.

The *X*-ray spectroscopy is useful to predict whether a chemical bond is covalent or ionic and the degree of covalency. We usually monitor the sharpness of the absorption maxima, edge shift of the principal absorption maximum, shift of the main absorption edge K, and the low energy peak for this purpose. Usually the ionic compounds exhibit sharp absorption maxima and the covalent compounds show somewhat broadened maxima. Accordingly, the cobalt(II) chloride hexahydrate exhibits a sharp maximum due to the $1s \rightarrow 4p$ transition and *N,N'*-tetramethylenebis(salicylideneimine)cobalt(II) and *N,N'*-hexamethylenebis(salicylideneimine)cobalt(II) show broadened (split) absorption maximum[7]. The latter two compounds thus, exhibit covalent character and cobalt(II) chloride hexahydrate shows ionic character. The shift of the principal K-absorption maximum to higher energy occurs if the compound is covalent. The energies of the principal absorption maximum (A) in several coordination compounds[10] are in the order: $[Cu(H_2O)_6]^{2+} < [Cu(NH_3)_4]^{2+} < [Cu(CN)_4]^{2-}$ and this indicates the increasing covalent character of the compounds. The *X*-ray K-absorption studies of several coordination compounds with a variety of ligands have lead also to the serialisation of ligands in order of increasing covalency in agreement with the nephelauxetic series[11]. The *X*-ray K-absorption measurements have been made to establish the relative covalent character of the M – S bond in coordination compounds. The main absorption edge shifts towards the high energy side and the shift decreases with the increase in covalency of the M – S bond. Thus, the bis(thiopropionic acid)copper(II) exhibits a larger shift (Δ = 7.0 eV) of the main absorption edge towards the higher energy in comparison to that of in bis(thiosalicylic acid)copper(II) (Δ = 5.1 eV), indicating that the Cu – S bond in the latter compound is more covalent[12]. A larger edge width is the characteristic of the presence of a greater degree of covalency. The presence of a larger edge width (13.9 eV) in bis(thiosalicylic acid)lead(II) in comparison to the smaller edge width (12.6 eV) in bis(thiopropionic acid)lead(II) signifies the presence of a greater degree of covalency in Pb – S bond in the former compound[13]. The presence of the low energy absorption maximum is more prominent where the chemical bond is more covalent. The appearance of the low energy absorption maximum in $[Ni(CN)_4]^{2-}$ and the absence of the low energy band in $[Ni(H_2O)_6]Cl_2$ indicate the presence of a greater degree of covalency[14,15] in $[Ni(CN)_4]^{2-}$.

Determination of valence state : The change in the valence state is associated with the change in the position of the principal absorption maximum (A) and the main absorption edge (K). The higher the oxidation state the greater are the shifts of the main absorption edge and the principal absorption maximum towards higher energies. However, the relative energy of the principal absorption maximum is a more reliable criterion than the shift of the main absroption edge for the determination of the oxidation states of the metal ions[16]. The *X*-ray K-absorption data of the following compounds have been used to determine the valence state of cobalt :

Main absorption edge (K) :	Co^0 (metal), 0 eV < $Co^{II}Cl_2.6H_2O$, 8 eV < (acetylacetonato) *N, N'*-trimethylenebis(salicylideneimine)cobalt(III), 18 eV[7].
Principal absorption maximum (A) :	Diaquo *N,N'*-trimethylenebis(salicylideneimine)cobalt(II), 17 eV < (acetylacetonato) *N, N'*-trimethylenebis(salicylideneimine)cobalt (III), 32 eV[7].

The assignments of the principal absorption maximum (A) in diaquo *N.N'*-trimethylenebis(salicylideneimine)cobalt(II) at 17 eV and in acetylacetonato *N,N'*-trimethylenebis(salicylideneimine)cobalt(III) at 32 eV to the $1s \rightarrow 4p$ and $1s \rightarrow 5p$ transitions, respectively are in accordance with the energy difference of the above transitions (17 eV and 30 eV)[7].

The valence of sulphur in tetrasulphur tetranitride, S_4N_4 has been determined by the *X*-ray emission spectroscopy[17]. The molecule has a cage structure (Fig. 7) with a square set of nitrogen

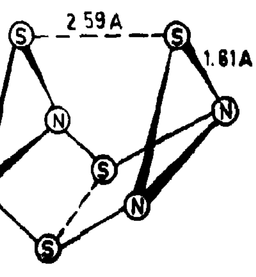


Fig. 7. Structure of N_4S_4 (D_{2d} symmetry).

atoms and a bisphenoid of sulphur atoms[18]. The *X*-ray emission spectrum of the compound exhibits a K_α doublet and the position of the doublet identifies the sulphur atom in S_4N_4 to possess the oxidation state +3. This is in contrast to the expectations of the classical valence theory of sulphur having two oxidation states, *viz.* +2 and +4 in S_4N_4. The *X*-ray spectroscopic data indicate that the electronic structure is a highly delocalised one and the electron distribution is evened out in the compound by delocalisation[17]. The S . . S and S . . S (linked by N) distances of 2.59 and 2.71Å, respectively also indicate the presence of a significant S – S interaction and S – S bonding[18].

The compounds or mixtures containing two oxidation states of a metal ion can also be characterised by the *X*-ray absorption and *X*-ray emission spectroscopy. The presence of the metal ion in two oxidation states has been found out from the observation of two distinct edges at different energies[19,20].

Determination of coordination stoichiometry : In coordination compounds of the ligands having many potential sites with different potential coordinating power, all the sites may not be utilised for coordination and this may lead to varied bonding which cannot sometimes be differentiated by the infrared spectroscopy due to the complexity of the infrared spectra arising out of the ligand absorptions. The *X*-ray K-absorption spectroscopy has been successfully applied for the determination of the coordination sites and for the differentiation of varied bonding. The *X*-ray K-absorption spectroscopy is specially useful for the determination of the coordination symmetry when the magnetic moment of the compound is inconclusive for the identification of the coordination symmetry. The spinel $Co[Al_2]O_4$ exhibits the room temperature magnetic moment of 4.9 B.M. and the assignment of the coordination symmetry unequivocally is not possible from the magnetic moment datum of the compound as the expected range of magnetic moments for the octahdral and tetrahedral cobalt(II) compounds are 4e7-5.2 and 4.4-4.8 B.M., respectively. But the *X*-ray K-absorption spectral data of the compound $C.o[Al_2]O_4$ indicate unambiguously the presence of a tetrahedral symmetry[21] in $Co[Al_2]O_4$. Usually the edge widths of the octahedral compounds are significantly lower than those of the tetrahedral compounds. In cobalt(II) compounds with the ligands containing oxygen donor sites, the edge width is usually in the range 5.0-7.6 eV for octahedral symmetry and 8.9-9.7 eV for tetrahedral symmetry.

The edge width can be calculated theoretically from the following equation[18].

$$\text{Edge width} = \frac{k^2}{\Sigma \mid \chi_M - \chi_L \mid}$$

where k is a constant and has the values 7.7, 8.5, 16.4, 19.1 for cobalt, copper, zirconium and niobium, respectively ; $\Sigma \mid \chi_M - \chi_L \mid$ is the sum of the metal atom and ligand atom electronegativity difference ; χ_M is the Pauling electronegativity of the metal atom ; and χ_L is the Pauling electronegativity of the ligand atom coordinated to the metal atom. A comparison of the observed and calculated edge widths of several compounds is presented in the Table 1 and the data show that it is possible to find out the coordination symmetry and metal-binding sites from the edge width studies.

TABLE 1—COMPARISON OF THE CALCULATED AND OBSERVED VALUES OF THE EDGE WIDTHS OF VARIOUS COBALT(II) AND COPPER(II) COMPOUNDS

Compound	Coordination stoichiometry	$\Sigma \mid \chi_M - \chi_L \mid$	Edge width Observed (Calculated) eV	Ref.
Co(salbn)[a]	CoN_2O_2	5.8	10.0 (10.2)	7
	CoN_4	4.8	10.0 (12.3)	
$CoCl_2.6H_2O$	CoO_6	10.2	5.6 (5.0)	7
$Co[Al_2]O_4$	CoO_4	6.8	8.9 (8.7)	21
$CuSO_4.5H_2O$	CuO_6	9.6	7.6 (7.5)	13
$Cu(CH_3COO)_2.H_2O$	CuO_5	8.0	8.4 (8.0)	22

[a]salbn = dianion of *N,N'*-tetramethylenebis(salicylideneimine).

Determination of the metal-ligand and metal-metal bond lengths :

The average radius (*R*) of the coordination sphere in the coordination compounds can be calculated using the formula[23]

$$R = \left(\frac{150}{\Delta E}\right)^{\frac{1}{2}}$$

where ΔE is the energy separation between the absorption maximum (B) and minimum (β) (Fig. 3). Due to the effect of crystal field on the absorbing ions, the splitting of the bands in the region B-β occurs and individual metal-ligand bond lengths can be calculated using the energy differences B-β, B'-β, B-B' and β'-β. The metal-ligand bond length data presented in the Table 2 agree well with the bond length data obtained from the single crystal *X*-ray studies. Thus, the extended *X*-ray K-absorption fine structure analysis can be used as a supplement for *X*-ray diffraction method.

The splitting of the principal absorption maximum to two distinct maxima occurs due to the presence of unequal metal-ligand bond lengths. The observation of this splitting in both the magnetically dilute and magnetically concentrated coordination compounds indicates that it is not the characteristic of the presence of magnetic exchange interaction. However, the agreement of the M – M data obtained from the *X*-ray K-absorption data and those of the *X*-ray diffraction data (Table 2) signifies the importance of the *X*-ray K-absorption spectroscopy in magnetochemistry. Although it is not possible to detect the presence of magnetic exchange from the room temperature magnetic moment data of copper(II) coordination compounds with normal magnetic moments, this can be detected by calculating the Cu – Cu bond distance from the *X*-ray K-absorption data. The presence of ferromagnetism in Ni metal has also been detected by the *X*-ray K-absorption spectral studies[17]. The application of this methodology for the determination of the nature of bond and metal-ligand bond length in rubredoxin, an iron containing protein of bioinorganic interest has been demonstrated in Table 2.

The observation of fine structure (Fig. 3) on the high energy side of the *X*-ray K-absorption edge is

TABLE 2—VALUES OF METAL-LIGAND AND METAL-METAL BOND LENGTHS OF VARIOUS COBALT, COPPER AND IRON COMPOUNDS FROM *X*-RAY K-ABSORPTION SPECTROSCOPY AND SINGLE CRYSTAL *X*-RAY DIFFRACTION DATA

Compound	ΔE eV	Bond length Å		Bond nature	Ref.
		X-Ray K-absorption	*X*-Ray diffraction		
Co metal	B-β=22	2.50	2.50	Co–Co	7
$CoCl_2.6H_2O$	B-β=25	2.45		Co–O	7
Co(salbn)[a]	B-β=42	1.90		Co–O	7
Cu(hippuric acid)$_2$.4H_2O	B-β=38.8	1.98	2.00	Cu–OH_2	24
			1.92	Cu–OOC	
	B′-β=10.8	3.20	3.30	Cu–Cu	
Cu(aminobutyric acid)$_2$.4H_2O	B-β=87.5	2.00	2.00	Cu–O	24
	B′-β=19.9	2.75	1.99	Cu–N	
Rubredoxin		2.24	2.24	Fe–S	41

[a]Abbreviation as in Table 1.

due to the scattering in the vicinity of the absorbing atom and the fine structure can be explained by considering the immediate environment surrounding the absorbing atom. The analyses of fine structure and edge width have made the *X*-ray K-absorption spectroscopy a potentially powerful tool for the determination of microscopic structure, metal-ligand and metal-metal bond lengths.

Qualitative and quantitative analysis of elements : The *X*-ray spectroscopy can not only detect qualitatively the presence of the elements but it can also be used for the quantitative estimation of the elements. The beauty and power of the *X*-ray spectroscopy have been to detect and analyse very small quantities of elements[25], even upto 0.0001% and several elements can be quantitatively determined in alloys and minerals simultaneously. The *X*-ray spectroscopy has taken an important position as an instrumental method of analysis capable of precise, selective, and the most importantly non-destructive elemental determinations. It has led the field in taking the advantage of computers and mathematics for the rapid determination of spectral data and reduction of requirements for calibration of standards. In the usual chemical analyses of elements we usually determine the percentages of carbon, hydrogen, and nitrogen, and leave the amount of oxygen which is often calculated by difference from 100%. The estimation of oxygen by the *X*-ray spectroscopy allows the elemental analysis upto 100% without going through the difference calculation for oxygen. Very small amount of samples can be analysed and the speed and precision of analysis by the *X*-ray spectroscopy are better than with the wet chemical techniques of analyses. The quantitative analyses of FeO in F_2O_3 and Al, Si, Mg in lunar rocks by the *X*-ray spectroscopy have been reported[20,27]. The oxidation state of the elements are critical with the titrimetric or colorimetric determination, but not with the *X*-ray spectroscopic method. The presence of the mineral sinoite (silicon oxynitride) has been found out in a meteorite sample and the elements (Si, O and N) have been quantitatively determined[28]. The detection of nitrogen in this sample indicates the presence of nitrogen in the environment in which the mineral is formed[28] and illustrates the importance of the *X*-ray spectroscopic analysis. The *X*-ray spectroscopy has been successfully used for the analyses of air and water pollution, solid surfaces, catalysts, semiconductors, ores, slurry, cement, petroleum, coal, trace elements in medicine and biological fluids, and for the determination of the thickness of layer(s)[29-38]. The samples used for *X*-ray spectral measurements are non-destructive and may be brought to the court as evidence in prosecuting violators of pollution laws.

Analysis of man-made high-temperature plasma : The distribution in man-made high-temperature plasmas has been found out by the *X*-ray spectroscopic analysis[39-40].

In conclusion, we would like to indicate that the chemical applications of the *X*-ray spectroscopy are almost unlimited. Enough examples have been cited to unfold the power and beauty of the *X*-ray spectroscopy in solving the physico-chemical problems of interests to chemists. There is no doubt that the *X*-ray spectroscopy will continue to solve more problems related to the discipline of chemistry. The future promise of this methodology is bright and the *X*-ray spectroscopy will no doubt occupy an important place among the more powerful methods for the determination of structures of molecules and nature of chemical bond in materials.

Acknowledgement

The author is grateful to the University Grants Commission, New Delhi, the Council of Scientific and Industrial Research, New Delhi, and the Department of Atomic Energy, Bombay for financial assistance.

References

1. W. L. BAUN and D. W. FISHER, *Nature (London)*, 1964, **204**, 642.
2. W. L. BAUN and D. W. FISHER, *Phys. Lett.*, 1964, **13**, 36.
3. D. W. FISHER and W. L. BAUN, *J. Appl. Phys.*, 1965, 36, 534.
4. D. W. FISHER and W. L. BAUN, *Spectrochim. Acta*, 1965, **21**, 443.
5. D. W. FISHER and W. L. BAUN, *Phys. Rev.*, 1966, **145**, 555.
6. N. V. BHAT and A. SYAMAL, *J. Mol. Struct.*, 1976, **30**, 161.
7. N. V. BHAT, A. SYAMAL, S. V. SALVI and P. H. UMADIKAR, *Spectrochim. Acta*, 1980, **35B**, 489.
8. A. SYAMAL, *J. Chem. Educt.*, in the press.
9. D. F. GUTTERMAN and H. B. GRAY, *J. Am. Chem. Soc.*, 1971, **93**, 3364.
10. W. W. BEAMAN and J. A. BEARDEN, *Phys. Rev.*, 1942, **61**, 455.
11. H. L. NIGAM and U. C. SRIVASTAVA, *Inorg. Chim. Acta*, 1971, **5**, 338.
12. U. C. SRIVASTAVA, H. L. NIGAM and A. N. VISHNOI, *Indian J. Pure Appl. Phys.*, 1972, **10**, 61.
13. H. L. NIGAM and U. C. SRIVASTAVA, *Chem. Commun.*, 1971, **14**, 761.
14. G. MITCHELL and W. W. BEAMAN, *J. Chem. Phys.*, 1952, **20**, 1298.
15. H. P. HANSON, "Developments in Applied Spectroscopy", Plenum Press, New York, 1968, Vol. 2, p. 254.

16. J. PRASAD, H. L. NIGAM and U. AGRAWALA, *J. Phys. C.*, 1976, **9**, 4949.
17. A. FAESSLER, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 34.
18. P. S. BRATERMAN, *J. Chem. Soc.*, 1965, **2297**.
19. E. VAINSHTEEN, R. M. OVRUTSKAYA, B. I. KOTLYAR and U. B. LINDE, *Sov. Phys. Solid State*, 1961, **5**, 2150.
20. P. W. ZINGARO and J. F. CROKE, Paper presented at the Mid-America Symposium in Spectroscopy, Chicago, 1967.
21. R. O. KEELING, JR., "Developments in Applied Spectroscopy", Plenum Press, New York, 1963, Vol **2**, p. 268.
22. U. C. SRIVASTAVA and H. L. NIGAM, *Indian J. Chem.*, 1971, **9**, 1301.
23. R. M. LEVY, *J. Chem. Phys.*, 1965, **43**, 1846.
24. A. KUMAR, C. B. BHARGAVA, A. N. VISHNOI, B. K. AGARWAL, M. N. SRIVASTAVA and U. C. SRIVASTAVA, *Transition Met. Chem.*, 1982, **7**, 121.
25. L. I. POLIZHAEVA, *Mater. Geol. Metallogen. Kol'sk. Poluostrova*, 1971, No. 2, 271 (*Chem. Abstr.*, 1972, **77**, 28020).
26. M. A. BLOKHIN, "*X*-ray Spectroscopy", Hindustan Publishing Corporation, New Delhi, 1962, p. 455.
27. I. ADLER and J. I. TROMBKA, *IEEE Trans. Nucl. Sci.*, 1973, **20**, 24.
28. C. A. ANDERSON K. KEIL and B. MASON, *Science*, 1964, **146**, 256.
29. M. A. BLOKHIN, "*X*-ray Spectroscopy", Hindustan Publishing Corporation, New Delhi, 1962, p. 466.
30. R. L. PARK and J. E. HOUSTON, *Adv. X-Ray Anal.*, 1972, **15**, 462.
31. V. VALOKOVIC, *Contemp. Phys.*, 1973, **14**, 439.
32. YU. M. GURVICH, A. N. MEZHEVICH, V. P. NICOLAEV, R. I. PLOTNIKOV, I. M. BOGACHEV and A. YA. SERBIN, *Zavod. Lab.*, 1974, **40** 665.
33. YU. G. LAVRENTEV, L. N. POSPELOVA, N. V. SOBOLEV and YU. I. MALIKEB, *Zavod. Lab.*, 1974, **40**, 657.
34. M. YOSHIMURA, *X-Ray Spectrom.*, 1975, **4**, 117.
35. T. J. KNEIP and G. R. LAURER, *Anal. Chem.*, 1972, **44**, 57A.
36. Y. GOHSHI, T. NAKAMURA and M. YOSHIMURA, *X-Ray Spectrom.*, 1975, **4**, 117.
37. A. N. OUSATINSKII, M. A. BUMIN and M. A. BLOKHER, *Dokl. Akad. Nauk SSSR*, 1977, **233**, 342.
38. F. W. LYTLE, *NBS Spec. Publ.* (*U.S.*), 1977, **475**, 34 (*Chem. Abstr.*, 1977, **86**, 195678).
39. M. R. LACAZE, O. BONNELLE and P. VALENTIN, *J. Phys.* (*Paris*), *Colloq.*, 1971, 57;(*Chem. Abstr.*, 1972, **77**, 11668).
40. D. J. NAGEL, *Adv. X-Ray Anal.*, 1975, **18**, 1.
41. R. G. SHULMAN, P. EISENBERGER, W. E. BLUMBURG and N. A. STOMBAUGH, *Proc. Natl. Acad. Sci. U.S.A.*, 1975, **72**, 4003.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 744-745

Some Complexes of Cobalt(II) and Nickel(II) with 2,5-Dihydroxyacetophenone Schiff Bases

G. P. POKHARIYAL*

Department of Chemistry, M. M. Degree College, Khekra-201 101

and

V. K. AGRAWAL, R. P. MAHESH and P. SINGH

Department of Chemistry, S. S. V. College, Hapur

Manuscript received 29 August 1981, revised 16 December 1983, accepted 10 August 1984

The composition of Co^{II} and Ni^{II} complexes with *N*-2,5-dihydroxyacetophenacylidene-2,5-dichloroaniline (DHAPADA) and *N*-2,5-dihydroxyacetophenacylidene-*p*-toluidine (DHAPAT) has been found to be 1 : 2 (M : L). Structural assessment of the complexes has been made on the basis of the results of magnetic moments, and electronic and ir spectral studies.

COMPLEXES of Co^{II} and Ni^{II} with ligands containing nitrogen and oxygen as donor atoms have been described in the literature[1-4]. The present communication reports the results of spectrophotometric studies of the complex formation of Co^{II} and Ni^{II} with DHAPADA and DHAPAT.

Experimental

All the chemicals used were of AR grade (B.D.H. or E. Merck). The Schiff bases, *N*-2,5-dihydroxyacetophenacylidene-2,5 dichloroaniline and *N*-2,5-dihydroxyacetophenacylidene-*p*-toluidine were prepared[5] by refluxing equimolar quantities of 2,5-dihydroxyacetophenone and 2,5-dichloroaniline/*p*-toluidine in ethanol for 4.5 h. The contents were cooled, filtered and the products washed with solvent ether (b.p. 60-80°). The products were crystallised from ethanol to give the compounds (decomp. points 94.5° and 122°).

Composition of complexes : Equimolar solutions of the metal chlorides ($CoCl_2$ or $NiCl_2$) and ligand (DHAPADA or DHAPAT) were mixed in the ratio 1 : 3, 1 : 2, 1 : 1 and 2 : 1, and the final volume was made upto 20 ml by adding the required amount of ethanol. The maximum absorption of the solutions was found to be 370 nm (with Co^{II}) and 520 nm (with Ni^{II}) in all the cases, indicating thereby, the formation of only one type of complex with the ligand.

The stoichiometry (M : L) of the complexes were determined by Job's method of continuous variation, molar ratio and slope ratio methods. The methods suggested 1 : 2 stoichiometry of the complexes which was further confirmed by conductometry and elemental analyses.

Isolation of the complexes : A mixture of metal chloride ($CoCl_2$ or $NiCl_2$) (20.0 ml, 0.02 *M*) and the ligand (40.0 ml, 0.02 *M*) in ratio 1 : 2 was refluxed in ethanol for 1 h. On cooling, brown or brown red crystals were deposited which were filtered, washed with water and dried *in vacuo*.

The metal chelates were found to be soluble in DMF and DMSO. The molar conductance value in DMF medium (10^{-3} *M*) 40 Ω^{-1} mol^{-1} cm^2, indicate a non-electrolytic nature of the complexes. Molecular weights of the complexes were determined cryoscopically using benzene as solvent and confirms the proposed composition of the complexes.

Magnetic susceptibility was measured by Gouy method using $Hg[Co(SCN)_4]$ as the calibrant. Electronic spectra (nujol) were recorded on a Cary-14 recording spectrophotometer. Infrared spectra (KBr) were obtained on a Perkin-Elmer model 521 spectrophotometer. The colour and elemental analyses are listed in Table 1.

Results and Discussion

Cobalt complexes : The observed magnetic moments for Co^{II} complexes (4.49 and 4.60 B.M.) are slightly less than the usual values for the high-spin octahedral cobalt complexes. This may be due to the incomplete quenching[6] of the orbitals of the metal ion during chelation leading to low-spin octahedral stereochemistry for the complexes.

The electronic spectra of the Co^{II} complexes (3) and (4) consist of two main bands appearing at 9000, 9550 and 23500, 24000 cm^{-1}, respectively. The highest and lowest energy bands are assigned to γ_3 and γ_1 transitions, whereas the two shoulders ${}^4T_{1g}(F) \rightarrow {}^2T_{1g}$, ${}^2T_{2g}$ (18650 and 18540 cm^{-1}, respectively) and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (20850 and 20600 cm^{-1}, respectively) either may be due to the splitting of γ_3 in many components or may be due to γ_2 transition[7]. The ratio γ_2/γ_1 for Co^{II} complexes in

octahedral fields was found[8-10] to lie in the range 1.80-2.20. However, for the present Co^{II} complexes (3) and (4), this ratio appear to be 2.07 and 1.94, respectively indicating thereby 20850 and 20600 cm^{-1} are due to ν_2 transition. The values of nephelauxetic ratio arising out of partial overlap of 3d orbitals with the σ and π orbitals of surrounding donors consist of both $f^2\sigma$ and $f^2\pi$, *i.e.* $f^2 = f^2\pi . f^2\sigma$ and are 1.13 and 1.19 for the complexes (3) and (4), respectively. Thus, the spectral data indicate a octahedral geometry for the Co^{II} complexes.

TABLE 1 — COLOUR AND ELEMENTAL ANALYSES DATA

Sl. no.	Compound	Colour	Analyses % ; Found/(Calcd.)*		
			N	Cl	Metal
1.	DHAPADA	Brown	4.60 (4.70)	28.72 (28.90)	—
2.	DHAPAT	Brown	5.72 (5.80)	—	—
3.	$[(DHAPADA)_2Co(H_2O)_2]$	Brown	4.12 (4.08)	20.90 (20.73)	8.52 (8.62)
4.	$[(DHAPAT)_2Co(H_2O)_2]$	Brown red	4.90 (4.87)	—	10.20 (10.24)
5.	$[(DHAPADA)_2Ni(H_2O)_2]$	Brown	4.17 (4 09)	20.90 (20.74)	8.67 (8 57)
6.	$[(DHAPAT)_2Ni(H_2O)_2]$	Brown red	4.80 (4.87)	—	10 26 (10.26)

*Satisfactory C and H analyses found.

Nickel complexes : The magnetic moment value (3.00 B.M.) observed for the Ni^{II} complex (6) is comparable with the assignment of octahedral configuration[11]. If in case of Ni^{II}, symmetry is allowed to be lower than cubic and if low-symmetry component is larger, then spin-paired term may be found in the neighboured[12]. At low temperatures it reaches diamagnetism whilst as the temperature increases, the magnetic moment approaches the spin-free value. *X*-Ray investigation[13,14] of paramagnetic (2.54 B.M.) bis-(mesostilbenediamine) nickel(II) dichloroacetate, has shown that crystal of this complex consists of a mixture of paramagnetic octahedral molecules and diamagnetic planar molecules. The subnormal magnetic moment (2.60 B.M.) observed for the complex (5) may be assumed to be intermediate between that of the low-spin state and high-spin state. It appears that the energy difference between the singlet and triplet is comparable with the thermal energy (kT). This has been possible due to the lowering of symmetry[15] from $O_h \rightarrow D_{4h}$. In octahedral complexes, the singlet state lies above triplet states. As the field along the Z-axis decreases, the triplet state comes closer to the singlet state, thus allowing partial thermal transition resulting in the decrease of magnetic moment.

Four bands have been observed in the electronic spectra of the complex (5) at 8000, 13000 (sh), 15200 and 26500 cm^{-1}. The latter two bands are characteristic of an octahedral complex[16], whereas the former two bands may be a consequence of ν_1 splitting due to low symmetry of the ligand field or due to the spin-forbidden transitions[17]. In the electronic spectra of complex (6), three spin-allowed bands at 9900, 16500 and 27500 cm^{-1} have been observed. The value of interelectronic repulsion parameter (β) comes out to be 953 cm^{-1} as against free-ion value[18] (1080 cm^{-1}). These observations suggest on octahedral symmetry for Ni^{II} complexes.

Ir spectral studies : The assignment of the inportant ir bands in the complexes has been compared with the spectrum of the free ligands. The ir spectrum of the ligands (DHAPADA and DHAPAT) show bands around 1600-1640 cm^{-1} (azomethine) and 3280-3300 cm^{-1} (phenolic OH). The metal complexes register lower values for azomethine ($\sim$1600 and 1560 cm^{-1}) indicating coordination of the ligand through azomethine nitrogen. The phenolic-OH stretching frequencies are also shifted to region 3250-3275 cm^{-1} on complexation with Co^{II} and Ni^{II}. This view is further supported by the appearance of bands corresponding to ν_{M-N} (530 cm^{-1}) and ν_{M-O} (450 cm^{-1}). The presence of coordinated water in all the complexes is indicated by bands around 3400(sh), 865 (w) and 700 cm^{-1} (w), assignable to OH stretching, rocking and wagging vibrations, respectively.

Acknowledgement

The authors wish to thank Dr. R. S. Kapil, C.D.R.I., Lucknow and Dr. M. N. Sharma, Principal, M. M. Degree College, Khekra for the help during investigations. The authors are also grateful to C.S.I.R., New Delhi for the award of Fellowship to one (V.K.A.) of them.

References

1. W. S. YAMADA, Y. KUGE and K. YAMANANOUCHI, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 1864.
2. J. C. BAILER and D. H. BUSCH, "The Chemistry of Coordination Compounds", Reinhold, New York, 1966.
3. Y. M. BRUCHER, *Nature (London)*, 1962, **194**, 885.
4. F. A. COTTON, D. M. L. GOODGAME and M. GOODGAME, *J. Am. Chem. Soc.*, 1961, **83**, 4690.
5. V. K. Agrawal, Ph.D. Thesis, Meerut University, 1980.
6. P. W. SALWOOD, "Magnetochemistry", Interscience, New York, 1958.
7. A. B. P. LEVER, *J. Chem. Soc.*, 1967, 2040.
8. A. WERNER, *Z. Anorg. Allg. Chem.*, 1893, **3**, 267.
9. A. A. SCHILT, *J. Am. Chem. Soc.*, 1960, **82**, 3000.
10. W. KLEM, *Z. Anorg. Allg. Chem.*, 1944, **252**, 225.
11. P. SINGH, V. SINGH, G. P. POKHARIYAL and K. B. S. CHAUHAN, *J. Indian Chem. Soc.*, 1980, **57**, 1025.
12. B. N. FIGGIS and J. LEWIS, *Prog. Inorg. Chem.*, 1964, **6**, 87.
13. W. E. BULL and L. E. MOORE, *J. Inorg. Nucl. Chem.*, 1965, **27**, 1341.
14. S. C. NYBURG and J. S. WOOD, *Inorg. Chem.*, 1964, **3**, 468.
15. W. C. E. HIGGINSON, S. C. NYBURG and J. S. WOOD, *Inorg. Chem.*, 1964, **3**, 468.
16. C. K. JORGENSEN, *Acta Chem. Scand.*, 1956, **10**, 887.
17. D. K. RASTOGI and K. C. SHARMA, *J. Inorg. Nucl. Chem.*, 1974, **36**, 222.
18. B. N. FIGGIS, "Introduction to Ligand Fields", Interscience, New York, 1966, p. 52.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 746-747

Chelating Ion-Exchangers Containing Thiosalicylamide as Functional Group for Separation of Platinum

A. DASGUPTA, M. MAJUMDAR and S. C. SHOME

Department of Chemistry, Presidency College, Calcutta-700 073

Manuscript received 24 August 1981, revised 30 April 1984, accepted 10 August 1984

Chelating ion-exchangers containing thiosalicylamide as functional group sorb Pt^{II} and Pt^{IV}. The preparation and properties of four such resins with different matrices are studied and the resin derived from polystyrene matrix crosslinked with 4% divinylbenzene is found to be the most effective for the separation and concentration of traces of platinum ions in aqueous solutions. Pt^{II} has been quantitatively separated from a number of commonly associated metal ions, e.g. Ru^{III}, Rh^{III}, Os^{VIII} and Ir^{III} by the use of the chelating resins.

THIOSALICYLAMIDE, (TSA), has shown selective action towards the platinum metal ions and forms strong chelates. Its incorporation in the resin matrices should, therefore, be of much practical interest in the separation and concentration of these metals. In the present work, four chelating resins incorporating TSA as the functional group have been prepared and their analytical properties investigated. Complying with the expectation Pt^{II} and Pt^{IV} are strongly sorbed by these chelating resins from hydrochloric acid as well as from acetate media. Pt^{IV}, however, is partially reduced by the resins in the acid solution and the reduction is facilitated with the decrease in acidity. Again, unlike Pt^{II}, the retained Pt^{IV} cannot be desorbed by any suitable eluent.

Experimental

Preparation of resins: Copolymerization of 0.2 mol *o*-nitrophenol (Resin I)/*p*-nitrophenol (Resin II) with 0.05 mol phenol and 0.5 mol formaldehyde in presence of 5 ml hydrochloric acid was carried out at 70°. The solid mass formed was further crosslinked with paraformaldehyde at 130°. The nitropolymer produced, was reduced to aminopolymer, which was subsequently diazotised and coupled with 0.2 mol TSA in 10% Na_2CO_3 solution.

The starting materials for resins III and IV were polystyrene—4% DVB copolymer and polystyrene—8% DVB copolymer, respectively. The nitration[1] and reduction of the copolymers were carried out and finally coupled with TSA, as given above. The resulting chelating resins were soxhleted with ethylalcohol, washed with *M* HCl and finally with deionized water.

Characterization of resins: The exchange capacities of the resins were measured in HCl medium (0.1-4.4 *M*) and also in the acetate buffer solution (*p*H 1.0-6.0) using standard platinum chloride solution (1.90 mg ml^{-1}). Equilibration rates of the resins for Pt^{II} and Pt^{IV} at the corresponding optimal acidities were also determined. The sorbed Pt^{II} ions were eluted with 0.5% KCN solution. As no suitable eluent was found out to desorb Pt^{IV}, excess unabsorbed Pt^{IV} was estimated and the amount of Pt^{IV} retained by the resin was obtained by difference. All the determinations of the metal ions were carried out with A.A.S.

Water regains of the resins were determined, after drying them at 100 for 48 h.

Estimation of nitrogen, sulphur and amino groups: Nitrogen contents of the nitro, amino and the final product were determined. Sulphur was estimated by barium sulphate method. Amino contents of the aminated copolymers were determined by nonaqueous titrimetry[2].

Column separation: A 50 cm glass column (1.1 cm i.d.) was packed with 5 g resin previously soaked in HCl. The effective bed volume was 7.5 ml. A solution (50 ml) containing a known amount of Pt^{II} and a diverse ion in *M* HCl, was passed through the resin column, preconditioned with *M* HCl. The resin bed was washed with *M* HCl. Pt^{II} was then eluted with 30 ml 0.5% KCN solution at flow rate of 1 ml min^{-1}.

Results and Discussion

All the resins have shown almost similar ability to sorb Pt^{II} and Pt^{IV} ions over a wide range of acidity. Both Pt^{II} and Pt^{IV} exhibit two maximum capacities. It has been found that with the decrease in acidity, the exchange capacity of the resins increases and reach a maximum at about 0.75 to 0.98 *M* acidity with respect to HCl, and then decreases. The exchange capacity again increases showing the maxima at *p*H 4.37 to 4.6. Among the prepared resins, the resin IV has shown maximum capacity for Pt^{II} (0.71 mmol g^{-1} of dry resin at 0.82 *M* HCl and 0.98 mmol at *p*H 4.38), and for Pt^{IV} (0.68 mmol

g^{-1} of dry resin at 0.80 *M* HCl, and 0.98 mmol at *p*H 4.38). The times for 50% sorption of the resin IV for Pt^{II} have been found to be lower at 0.82 *M* HCl (40 min) than at *p*H 4.38 (55 min). The greater equilibration rate of resin IV can be explained in terms of its macroporosity and maximum swelling property. (The water-regain values of resin I, II, III and IV are 0.60, 0.48, 0.42 and 1.18 g water/g resin, respectively). All the prepared resins exhibit reducing property which increases with decrease in the acidity. Pt^{IV} is partially reduced to Pt^{II} before its sorption with the resin.

Different eluents have been tried to desorb the retained Pt^{II} from the resin IV. Solutions of disodium salt of EDTA, potassium sodium tartrate, sodium citrate, orthophosphoric acid and *M* HCl failed to elute any Pt^{II} ions. 20% elution can, however, be effected with 12 *M* HCl, 7% with 2% thiourea solution, and 30% with 2% stannous chloride solution. However, 0.5% KCN solution can elute the sorbed Pt^{II} quantitatively.

The nitrogen content of the nitropolymer of resin IV is found to be 8.4%, and the amino derivative contains 9.63% total nitrogen and 6.75% amino nitrogen. The chelating resin, on analysis, gives 10.13% total nitrogen and 6.09% sulphur. Therefore, the dry resin IV contains 1.89 mmol of ligand nitrogen. However, the maximum exchange capacity of resin IV for Pt^{II} is found to be 0.98 mmol g^{-1} of dry resin. Steric factor is probably responsible for this low value.

Separation of platinum(II) ions with the resin IV : Resin IV has been chosen for column operation due to its better equilibration rate and higher exchange capacity. The retention and elution characteristics of a large number of co-ions have been examined. Zn^{II}, As^{III}, Al^{III}, Cr^{III}, Zr^{IV}, Ti^{IV}, Ga^{III}, In^{III}, Tl^{III}, Mn^{II}, Th^{IV}, U^{VI}, Ni^{II}, Co^{II}, Rh^{III} and Ir^{III} are not sorbed by the resin IV from any acidic solution. Cd^{II}, Bi^{III}, Se^{IV} and Te^{IV} are not sorbed by the resin from solutions in *M* HCl. It is thus possible to separate quantitatively Pt^{II} (5.7 mg or 11.4 μg) from mixtures containing 170 mg or 300 μg, respectively of each of the above mentioned metal ions in *M* HCl solution by circulating the solutions through the resin. The sorbed Pt^{II} is eluted with four bed volumes of 0.5% KCN solution. Fe^{III} is sorbed (0.027 mmol g^{-1} dry resin at *M* HCl) by the resin, which can be selectively eluted with (1 : 5) H_3PO_4. Ru^{III}, V^{V} and Os^{VIII}, when previously reduced by SO_2, are not sorbed at *M* HCl. Mo^{VI}, when reduced by SO_2, is however, slightly sorbed (0.014 mmol g^{-1} dry resin at *M* HCl). The sorbed molybdenum ions can be selectively eluted with four bed volumes of 5% potassium sodium tartrate solution. Macro or micro amounts of Pt^{II} have been effectively separated from Fe^{III}, Ru^{III}, V^{V}, Os^{VIII} and Mo^{VI} by the use of the aforesaid resin. The interferences of Au^{III}, Cu^{II}, Hg^{II} and Pd^{II}, however, cannot be avoided.

References

1. R. V. DAVIES, J. KENNEDY, E. S. LANE and J. L. WILLIAMS *J. Appl. Chem.*, 1959, 368.
2. G. E. FICKEN and E. S. LANE, *Anal. Chim. Acta*, 1957, **16**, 207.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 748-750

Electrostatic Effects in Some Lanthanide-EDTA-Alizarine Red Sulphonic Acid Ternary Complexes

S. N. LIMAYE and M. C. SAXENA*

Department of Chemistry, Dr. Harisingh Gour Vishwavidyalaya, Sagar-470 003

Manuscript received 28 June 1983, revised 13 March 1984, accepted 15 August 1984

A pH-metric study of 1 : 1 binary and 1 : 1 : 1 mixed-ligand complexes of La^{III}, Ce^{III}, Pr^{III}, Nd^{III} and Sm^{III} has been carried out in aqueous medium using EDTA as primary ligand and alizarine red sulphonic acid (ARS) as secondary ligand (H_2L) employing Irving-Rossotti titration technique, at 25° and ionic strength of 0.2 mol dm^{-3} $NaClO_4$. The effect of electrostatic repulsion between $[LN\text{-}EDTA]^-$ and L^{2-} species on the stability of the ternary complexes has been studied.

The general order of stability for the binary and ternary complexes is found to be $\log K^M_{MA} > \log K^M_{ML} > \log K^{MA}_{MAL}$, whereas the trend in $\log K^{MA}_{MAL}$ values with respect to metal ions is $La^{III} < Ce^{III} < Pr^{III} < Nd^{III} < Sm^{III}$. Validity of Born relation has been studied. The $\log K^{MA}_{MAL}$ values have been correlated with certain fundamental properties of lanthanides (LN), *viz.* standard entropies (S^0_M), standard oxidation potentials (E°), sum of the first three ionisation potentials (ΣI) and total angular momentum (L). Mathematical expression for the log-log correlations of $\log K^{MA}_{MAL}$ *vs* $\log K^M_{MA}$ has also been derived and discussed.

ALTHOUGH extensive work has been carried out spectrophotometrically on alizarine red sulphonic acid complexes but very few have been studied potentiometrically[1-4]. The present communication deals with the *p*H-metric studies of 1 : 1 binary and 1 : 1 : 1 mixed complexes of La^{III}, Ce^{III}, Pr^{III}, Nd^{III} and Sm^{III} using EDTA as primary ligand and alizarine red sulphonic acid (monosodium salt monohydrate ARS) as secondary ligand, employing Irving-Rossotti titration technique at 25° and ionic strength of 0.2 mol dm^{-3} $NaClO_4$.

Experimental

Standard solutions of lanthanide metal ions (LN^{3+}) were prepared by dissolving their nitrates of La^{III}, Ce^{III}, Sm^{III} in doubly distilled water. The oxides of Pr^{III} and Nd^{III} were dissolved in minimum quantity of perchloric acid, excess of which was successively evaporated. Disodium salt of EDTA was used. The two remaining protons were also taken into consideration. Usual titration sets for the study of 1 : 1 binary (ML or MA) and 1 : 1 : 1 mixed complexes (MAL) were prepared. Use of dilute solutions (10^{-3} mol dm^{-3}) was made to avoid the possibility of formation of polynuclear species. The sets were titrated against 0.2 mol dm^{-3} carbonate free NaOH and the *p*H was recorded on an Elico model LI-120 digital type *p*H-meter.

Results and Discussion

The values of metal-ligand stability constants of 1 : 1 binary ($\log K^M_{ML}$) and 1 : 1 : 1 ternary complexes ($\log K^{MA}_{MAL}$) as computed by Irving-Rossotti[5] *p*H-titration technique along with their $\Delta\log K$ ($\Delta\log K = \log K^{MA}_{MAL} - \log K^M_{ML}$), ΔG ($\Delta G = -2.303\ RT \log K^{MA}_{MAL}$) and $\log \beta^M_{MAL}$ ($\log \beta^M_{MAL} = \log K^M_{MA} + \log K^{MA}_{MAL}$, *i.e.* overall stability constant of the ternary complexes MAL) have been recorded in Table 1.

The ligand curve (not shown) indicates the liberation of two protons, one at *p*H 4.00 and the other at 10.50. The practical proton-ligand stability constants $\log K^H_n$ were calculated for $\bar{n}_H$ (formation function corresponding to proton-ligand formation constant) values lying in the range $0 < \bar{n}_H < 2$. The formation of mixed ligand complex, MAL takes place according to the equilibria $M + A \rightleftharpoons MA$; $MA + L \rightleftharpoons MAL$. Theoretical composite curve[6] was also drawn. The non-superimposable nature of the composite curve on the experimental mixed-complex curve indicates the formation of mixed-complex. The formation of mixed-complex takes place at the *p*H where the formation of hydroxo-species can be ignored. The plot of $\bar{n}/[L]$ *vs* $[L]$ (where $\bar{n}$ = formation function of the complex ML or MAL, and $[L]$ = free ligand exponent) is found to be smooth indicating the absence of polynuclear species.

TABLE 1—METAL-LIGAND STABILITY CONSTANTS OF 1 : 1 BINARY (log K^{M}_{ML}) AND 1 : 1 : 1 TERNARY (log K^{MA}_{MAL}) COMPLEXES, ΔG, Δ log K, log β^{M}_{MAL} VALUES FOR THE TERNARY LANTHANIDE-EDTA-ARS SYSTEMS*

I = 0.2 mol dm^{-3} NaClO$_4$ Temp. = 25°

	Metal ions				
	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}
log K^{M}_{ML}	9.98 (±0.04)	10.06 (±0.02)	10.09 (±0.08)	10.13 (±0.04)	10.21 (±0.01)
log K^{MA}_{MAL}	7.81 (±0.04)	7.97 (±0.02)	8.12 (±0.03)	8.21 (±0.04)	8.36 (±0.05)
−Δlog K	2.19	2.09	1.87	1.82	1.85
−ΔG(Kcal/mole)	10.72	10.94	11.15	11.26	11.47
log β^{M}_{MAL}	19.44	19.80	20.37	20.74	21.20

* The values of standard deviations for log K^{M}_{ML} and log K^{MA}_{MAL} are given in parentheses.

A perusal of the values of stability constants (Table 1) shows that the general trend of stability for the binary and ternary complexes is log K^{M}_{ML} > log K^{MA}_{MAL}. The values of log K^{MA}_{MAL} are obviously lower due to coulombic repulsion between the negatively charged primary complex [LN-EDTA]$^-$ and the incoming secondary ligand L^{2-}. The Δ log K values are, therefore, negative. Steric and statistical factors[7] are also expected to contribute towards lowering of log K^{MA}_{MAL} values as compared to log K^{M}_{ML}.

The order of stability with respect to metal ions for binary as well as ternary complexes has been found to be $La^{III} < Ce^{III} < Pr^{III} < Nd^{III} < Sm^{III}$, which is the order of their decreasing ionic radii.

In lanthanides the 4f^n electrons are well shielded from ligand perturbations by the outer 5s and 5p orbitals. The metal-ligand bond should, therefore, be ionic with minimal covalent contribution. Born relation[8], $E = Z^2/r\ [(1-1/D)]$ (where E = energy of complexation, Z = charge on metal ion, r = crystal radius of metal ion, D = dielectric constant of medium) has been tested for the present series of ternary complexes. Plots of log K^{M}_{ML} or log K^{MA}_{MAL} *vs* Z^2/r (Fig. 1) are slightly curved, which may be due to partial covalent nature[9] of the bond and varying degrees of stabilisation caused due to ligand field. Similar observations have been noted[10-13] for other lanthanide complexes.

The log K^{M}_{ML} and log K^{MA}_{MAL} values have been correlated with some fundamental properties of lanthanides, *viz*. standard entropies (S^{0}_{M}), standard oxidation potentials (E°), sum of the first three ionisation potentials (ΣI) and total angular momentum (L).

A linear variation of log K^{MA}_{MAL} and log K^{M}_{ML} with S^{0}_{M} (Fig. 1) indicates that the free energy changes during complexation are essentially entropy changes.

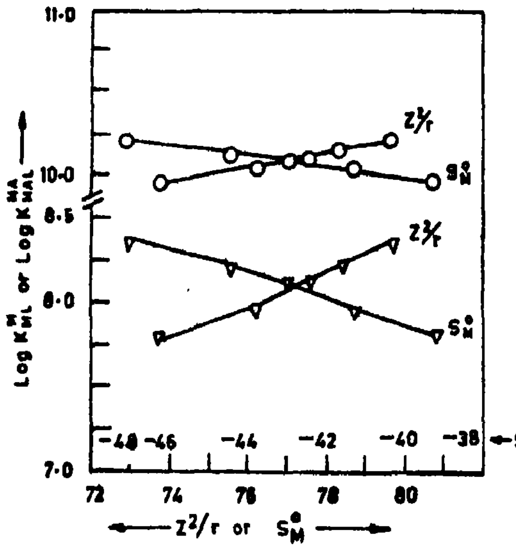


Fig. 1. Log K^{M}_{ML} (O) and log K^{MA}_{MAL} (▼) *vs* Z^2/r and S^{0}_{M} values of lanthanide metal ions.

A similar trend has been observed for 1 : 1 LN-EDTA complexes[14]. The standard electrode potentials (E°) of the lanthanides used when plotted against the stability constants yield a linear plot (Fig. 2). The free energy change corresponding to the standard electrode potentials comprises mainly the heat of formation of the bare lanthanide metal ion and its heat of hydration, the latter being the heat of ligation of water molecules, one may expect a gradual increase in log K values with decrease in E° values for lanthanides.

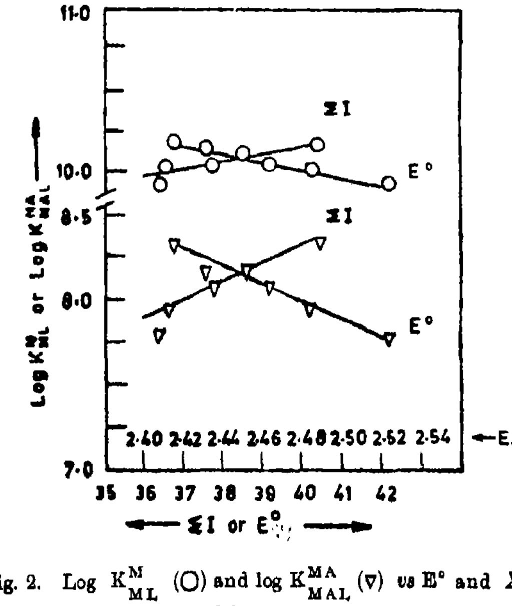


Fig. 2. Log K^{M}_{ML} (O) and log K^{MA}_{MAL} (∇) *vs* E° and ΣI of lanthanide metal ions.

The ionisation potentials may be regarded as a measure of electron affinity and a direct correlation

between the stability constants (log K^{MA}_{MAL} or log K^{M}_{ML}) and the overall ionisation potential (ΣI) of the lanthanides may be possible. Fig. 2 shows that the plots of log K *vs* ΣI are linear. La^{III} falls below the line in each case as its ΣI value lies relatively closer to that of Ce^{III}.

Recently, attempt has been made[15] to explain the so-called 'Gd-break' (also double-double effect[16,17] or tetrad effect[18,19]) by correlating the stability constants of complexes and several other properties of the lanthanides with the numerical values of their total angular momentum (L). These plots were four segmented inclined 'W' (i.e., $\leqq$) type for the entire series from La^{III} to Lu^{III}. Fig. 3 shows the inclined 'W' plots of log K^{M}_{ML} and log K^{MA}_{MAL} *vs* L. Only the first segment is possible in the present case. The plots are almost linear. The validity of the results has been further tested by drawing log-log plots of log K^{MA}_{MAL} *vs* log K^{M}_{MA}. Mathematical expression derived for this correlation[20] is,

$$\text{Log } K^{MA}_{MAL} = \log K^{M}_{MA} + (2.303RT)^{-1} [G^{0}_{L} - G^{0}_{A}) + (2G^{0}_{MA} - G^{0}_{MAL} - G^{0}_{M})].$$

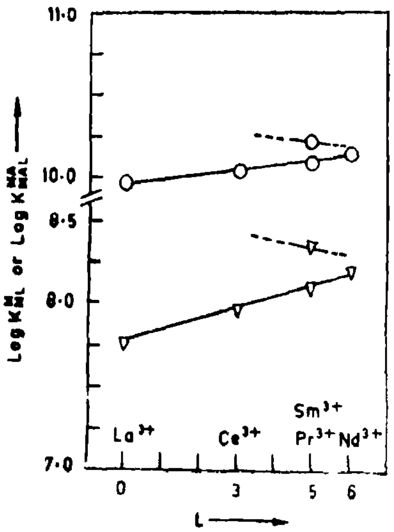


Fig. 3. Log K^{M}_{ML} (O) or log K^{MA}_{MAL} (∇) *vs* L values of lanthanide metal ions (L = total angular momentum of lanthanide metal ions).

From the expression log K^{MA}_{MAL} is expected to vary linearly with log K^{M}_{MA} provided the first term within brackets on the right hand side is constant and the second term is either negligible in comparison to the first term or constant or a linear function of log K^{M}_{MA}. The first two conditions will lead to a plot of unit slope and the third to a non-unit slope. The best straight line plot drawn by using the method of least squares gives the equation,

$$\log K^{MA}_{MAL} = 0.39 \log K^{M}_{MA} - 0.86.$$

Yatsimirskii and Kostromina[21] have calculated extrastabilistion energy (*i.e.*, l.f.s.e.) for the 1 : 1 binary LN-EDTA chelates considering them to be octahedral. Although such a procedure would lead to somewhat approximate values, but it gives an idea of the order of magnitude of l.f.s.e. in solution. The values of l.f.s.e. and 14 Dq in the present series have been calculated using the same procedure. The maximum value of 14 Dq corresponds to 140 cm^{-1} which is less than the values obtained from spectroscopic measurements[22]. It has been shown[23] that the electron pairing energy in $^{4}2_{u}$ sub-level in lanthanides is about 8000 cm^{-1}, which is much higher than the maximum value of l.f.s.e. in the present case. This will thus favour only a 'high-spin' distribution of electrons in LN-EDTA chelates.

Acknowledgement

The authors are thankful to Prof. A. V. Mahajani for providing laboratory facilities. One of the authors (S.N.L.) is thankful to the U.G.C., New Delhi for the award of a Senior Research Fellowship.

References

1. E. M. Larson and S. T. Hirazova, *J. Inorg. Nucl. Chem.*, 1956, **3**, 198.
2. S. K. Banerji and A. K. Dey, *J. Sci. Ind. Res., Sect. B.*, 1961, **20**, 375.
3. A. Varadrajulu and U. V. Seshaiah, *J. Indian Chem. Soc.*, 1971, **48**, 1065.
4. D. G. Marathe and K. N. Munshi, *J. Indian Chem. Soc.*, 1982, **59**, 617.
5. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904 ; 1953, 3397.
6. G. H. Carey and A. E. Martell, *J. Am Chem. Soc.*, 1967, **85**, 885.
7. J. L. Hoard, B. Lee and M. I. Lind, *J. Am. Chem. Soc.*, 1965, **87**, 1612.
8. T. D. Moeller, *Chem. Rev.*, 1965, **65**, 1.
9. F. J. Spedding, J. E. Powell and E. J. Wheelwright, *J. Am. Chem. Soc.*, 1956, **78**, 34
10. L. K. A. Staveley and T. Randall, *Faraday Discuss. Chem. Soc.*, 1958, **26**, 157.
11. G. P. Sengupta and C. R. Bera, *J. Indian Chem. Soc.*, 1980, **57**, 558.
12. M. S. Mayadeo and S. S. Purohit, *J. Indian Chem. Soc.*, 1980, **57**, 1047.
13. S. N. Limaye and M. C. Saxena, *J. Indian Chem. Soc.*, 1982, **59**, 698, 916.
14. J. K. Foreman and T. D. Smith, *J. Chem. Soc.*, 1957, 1752.
15. S. P. Sinha, *Helv. Chim. Acta*, 1975, **58**, 1978.
16. I. Fidelis, *Bull. Acad. Pol. Sci.*, 1970, **18**, 681.
17. I. Fidelis, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3191.
18. L. J. Nugent, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3485.
19. D. F. Peppard and G. W. Mason, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2271 , 1970, **30**, 339.
20. S. N. Limaye, Ph.D. Thesis, Dr. Hari Singh Gour Vishwavidyalaya, 1983.
21. K. B. Yatsimirskii and N. A. Kostromina, *Russ. J. Inorg. Chem.*, (*Engl. Transl.*), 1964, **9**, 971.
22. L. Holleck and D. Eckardt, *Z. Naturforsch.*, 1952, **10**, 660.
23. J. S. Griffith and L. E. Orgel, *J. Chem. Phys.*, 1957, **26**, 988.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 751-756

Kinetics of Oxidation of Hydroxyl Ion by Potassium Hexacyanoferrate(III)

K. V. C. RAO*, S. K. NEMA, V. N. KRISHNAMURTHY, V. SWAMINATHAN and V. R. GOWARIKER

Inter-Disciplinary Research Group, Vikram Sarabhai Space Centre, Trivandrum-695 022

Manuscript received 23 February 1983, revised 16 February 1984, accepted 10 August 1984

The kinetics of the oxidation of hydroxyl ion in solution by potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$ with an applied voltage potential of 0.45 V have been studied and reported in this paper. The effects of hexacyanoferrate ion concentration, pH, and applied voltage at room temperature on the evolution of oxygen are investigated and a probable mechanism for the oxidation reaction is suggested.

IT is reported in the literature[1,2] that potassium hydroxide reacts with potassium hexacyanoferrate(III) in solution, evolving oxygen according to equation (1).

$$2K_3[Fe(CN)_6]+2KOH \rightarrow 2K_4[Fe(CN)_6]+H_2O+\tfrac{1}{2}O_2 \quad (1)$$

The same reaction, however, does not take place when dilute solutions of potassium hydroxide and potassium hexacyanoferrate(III) solutions are mixed. Moreover, hexacyanoferrate(III) solutions are quite stable in alkaline medium, since thermodynamically the reaction is endothermic with an oxidation potential of 0.46 eV according to the equations

$$[Fe(CN)_6]^{3-}+e \rightarrow [Fe(CN)_6]^{4-}+0.37 \text{ eV} \quad (2)$$

$$2OH^- \rightarrow H_2O+e+\tfrac{1}{2}O_2-0.83 \text{ eV} \quad (3)$$

or

$$[Fe(CN)_6]^{3-}+2OH^- \rightarrow [Fe(CN)_6]^{4-}+H_2O+\tfrac{1}{2}O_2-0.46 \text{ eV} \quad (4)$$

It is, however, observed that oxygen evolution does take place when a pellet of potassium hydroxide is added to a solution of potassium hexacyanoferrate(III) ($\sim 0.1M$). This suggests that a localised concentration of hydroxyl ions is essential for the evolution of oxygen in the above system. A potential is applied to simulate the localised concentration at the anode for oxygen evolution. The present paper is concerned with the effect of initial concentration of the reactants, temperature, and external potential on the evolution of oxygen in the above system.

Experimental

Potassium hexacyanoferrate(III) and potassium hydroxide used in the experiments were of AnalaR grade. The solutions used were made from distilled water.

A three-necked flask (250 ml) with two platinum electrodes fused at the bottom was used as a cell for carrying out the experiment as shown in Fig. 1. Through one of the necks was connected a burette closed with a rubber septum for collecting the evolved oxygen, while through the second, a combined electrode for measuring pH of the solution was housed.

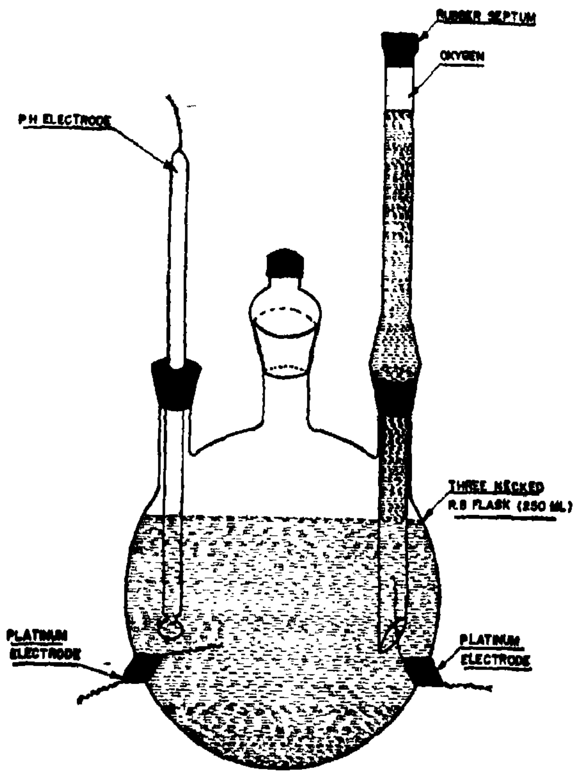


Fig. 1. Experimental set up (reaction cell).

The pH of the solution was monitored at 30° using a combined electrode digital Global model no. DPH 500 pH meter after disconnecting the cell. The oxygen gas was identified using a Schimadzu model 5A gas chromatograph with molecular sieve 5A column and helium as carrier gas. DC potential

was applied using Aplab Regulated Power Supply Unit Type LVA 65/5.

Equal quantities of potassium hexacyanoferrate(III) and potassium hydroxide solutions at different concentrations were mixed in the above reaction cell. A known potential was applied between the two platinum electrodes. The *p*H of the solution, the amount of oxygen evolved, and the concentration of hexacyanoferrate(III) were measured at different intervals of time. The hexacyanoferrate(III) concentration was estimated iodometrically[8].

The experiments were carried out at different temperatures, *viz.* 27, 35, 45 and 55°. The initial concentrations of hexacyanoferrate(III) used in the experiments were in the range 0.02 to 0.5 *M*. The variation of *p*H considered in the experiment was from 9 to 13.7 (Fig. 3), while the applied potential was varied from 0.2 to 1.2 V.

Results and Discussion

Variation of oxygen evolution rate with initial concentration of hexacyanoferrate(III) : The data on the rate of oxygen evolution at constant potentials of 0.6 and 0.45 V and *p*H of 13.1 at 27°, varying the initial concentration of hexacyanoferrate(III) from 0.05 to 0.4 *M*, are exhibited in Fig. 2. It is observed that under these conditions, the rate of oxygen evolution increases linearly with the initial concentration of hexacyanoferrate(III) according to the equation (5).

$$\frac{d[O_2]}{dt} = K_3[Fe(CN)_6]^{3-} \tag{5}$$

The value of K_3 (Fig. 2) is found to be approximately 0.24 ml/(h *M*) for 0.6 V and 0.08 ml/(h *M*) for 0.45 V.

Variation of oxygen evolution rate with pH : The variation of oxygen evolution with *p*H at constant hexacyanoferrate(III) concentration (0.5 *M*) at 27° and at an applied potential of 0.48 V is described in Fig. 3. As can be easily noted from the figure, the logarithm of the rate of oxygen evolution increases approximately linearly with *p*H having a slope of 1.4. In other words,

$$\log \frac{[d(O_2)]}{dt} = 1.4\ pH + K_4 \tag{6}$$

Substituting for *p*H and simplifying further, we obtain

$$\frac{[d(O_2)]}{dt} = K_5[OH]^{1.4} \tag{7}$$

This indicates that the rate of oxygen evolution is dependent on hydroxyl ion concentration but oxygen is directly evolved in a single step. Probably first an electron transfer reaction takes place giving hydroxyl radical which subsequently reacts to give oxygen according to equations (8) and (9).

$$[Fe(CN)_6]^{3-} + OH^- \rightarrow [Fe(CN)_6]^{4-} + OH^\cdot \tag{8}$$

$$2OH^\cdot \rightarrow H_2O + \tfrac{1}{2}O_2 \tag{9}$$

Variation of oxygen evolution rate with temperature : Table 1 presents the variation of the rate of oxygen evolution with temperature at constant potential 0.91 V and *p*H 13.35 with an initial con-

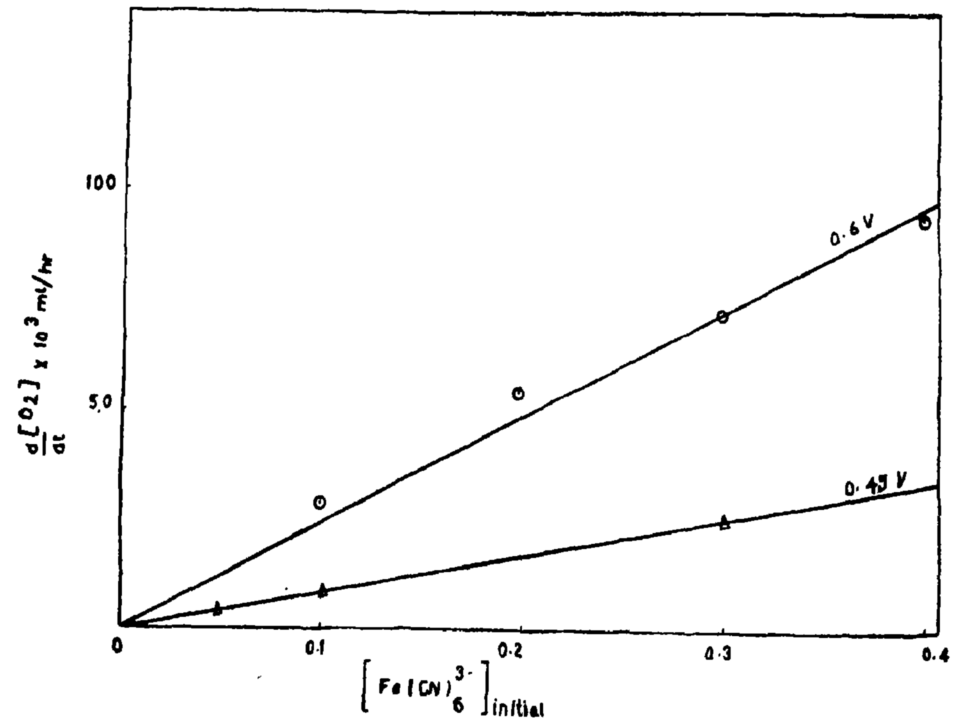


Fig. 2. Variation of the rate of oxygen evolution with the initial hexacyanoferrate(III) concentration at constant temperature and applied voltage.

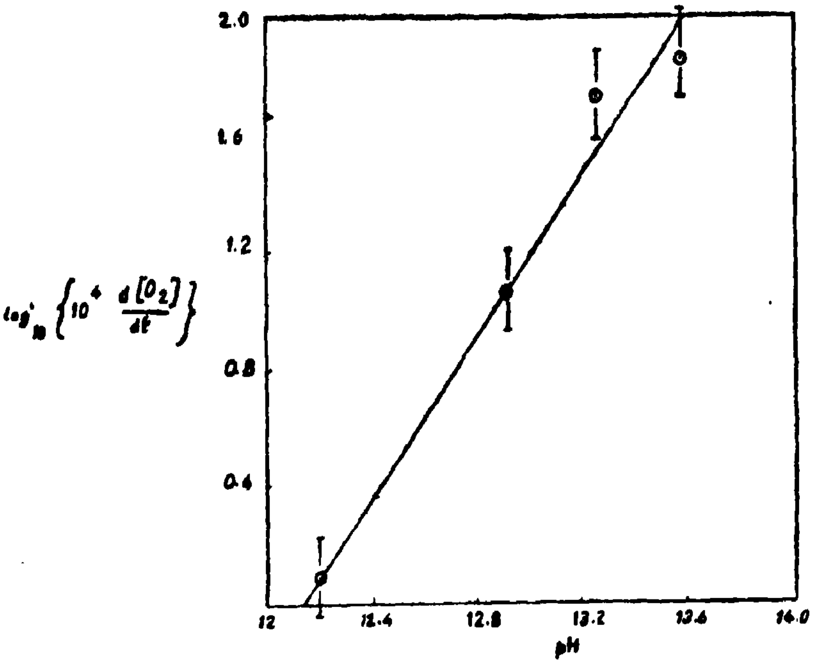


Fig. 3 Variation of oxygen evolution with pH at constant hexacyanoferrate(III) concentration.

centration of hexacyanoferrate(III) 0.25 M. Table 1 reveals that the rate of evolution of oxygen decreases with increase of temperature. This decrease is possibly attributable to the fact that the organised layer of the ions is disturbed by an increase in the temperature.

TABLE 1 – VARIATION OF RATE OF OXYGEN EVOLUTION WITH TEMPERATURE

Temperature °C	Rate of oxygen evolution $\times 10^{-6}$ mole sec^{-1}
35	0.87
45	0.55
55	0.22

Variation of oxygen evolution rate with applied potential : Table 2 presents the trends in the variation of oxygen evolution rate with applied potential at constant pH, initial hexacyanoferrate(III) concentration and temperature. The Table 2 reveals that an increase in the applied voltage or the initial concentration is accompanied by an increase in the rate of oxygen evolution.

TABLE 2 – VARIATION OF OXYGEN EVOLUTION RATE WITH APPLIED POTENTIAL AND INITIAL HEXACYANOFERRATE CONCENTRATION

Initial concentration M	Voltage V	Rate of oxygen evolution $\times 10^{3}$ ml h^{-1}
0.05	0.45	4.5
0.05	0.6	8.8
0.1	0.45	9.5
0.1	0.6	27.7

Remarks on nature of oxygen evolution reaction : It also appears from the oxygen evolution reaction in alkaline hexacyanoferrate(III) solution with a given potential that the reaction is not electrochemical, as conjugate reaction at cathode could not be identified. The concentration changes in the constituents around the cathode [hydroxyl ion, hexacyanoferrate(III)], hexacyanoferrate(II) remain constant without evolving hydrogen, while around the anode there is a change in the pH, hexacyanoferrate(III and II) concentration and evolution of oxygen which is observed to be continuous. This led us to infer that in the cell, around the anode, hexacyanoferrate(III) ions and hydroxyl ions are accumulating due to electrostatic force of attraction resulting in a concentration zone, similar to the one observed in the case of solid potassium hydroxide and hexacyanoferrate(III) system. To verify this assumption experimentally, hexacyanoferrate(III) concentration changes in the two systems, *viz*. solid potassium hydroxide-hexacyanoferrate(III) solution and alkaline hexacyanoferrate(III) solution with potential, were measured while evolving the same quantity of oxygen (about 4.5 ml). The concentration changes of hexacyanoferrate(III) in the two systems to evolve the oxygen are comparable when a correction is applied for the side reaction in the case of solid potassium hydroxide-hexacyanoferrate(III) solution and the details of the experimental results are given in Table 3.

Kinetics of reaction : With a view to assessing the individual order of the reaction with respect to hexacyanoferrate(III) and hydroxyl ion concentration, plots of their concentrations against time are drawn

and given in Figs. 4, 5 and 6. It is easy to see that the rates are first order with reference to total hexacyanoferrate(III) and hydroxyl ions. To assess the overall reaction, a plot of log (a − x)/(b − x) *vs* time was drawn (Fig. 7), where a is the initial hexacyanoferrate(III) concentration and b is the initial hydroxyl ion concentration. The straight line confirms that the overall reaction is second order. It is, however, noted from Table 3 that for one mole of oxygen evolved, 6.9 moles of hexacyanoferrate(III) is consumed. This implies that hexacyanoferrate(III) is not only consumed for oxygen evolution but also in a side reaction, probably in the hydrolysis reaction.

TABLE 3—DETAILS OF EXPERIMENTAL RESULTS

Sl. no.	Parameter	Solid KOH-hexacyanoferrate(III)	Alkaline hexacyanoferrate(III) solution with applied potential
1.	Initial concentration of ferrate(III)	8.11×10^{-3} mol/60 ml	3.22×10^{-3}
2.	Final concentration of ferrate(III)	2.93×10^{-4} mol/60 ml	3.09×10^{-3}
3.	Ferrate(III) consumed	1.73×10^{-3} mol/60 ml	1.27×10^{-3}
4.	Oxygen evolved	1.73×10^{-4} mol	1.85×10^{-4}
5.	Hexacyanoferrate(II) evolved	9.82×10^{-4} mol	8.99×10^{-4}
6.	Ratio of 4 to 3	1 : 10	1 : 6.9
7.	Ratio of 4 to 5	1 : 5.7	1 : 4.7

$$[Fe(CN)_6]^{3-} + OH^- \rightarrow Fe(CN)_5OH + CN^- \quad (9)$$

$$[Fe(CN)_5OH]^{3-} + OH^- \rightarrow Fe(CN)_4OH_2 + CN^- \quad (10)$$

$$[Fe(CN)_4OH_2]^{3-} + OH^- \rightarrow Fe(CN)_3OH_3 + CN^- \quad (11)$$

$$[Fe(CN)_3OH_3]^{3-} \rightarrow Fe(OH)_3 + 3CN^- \quad (12)$$

The fact that the reaction is first order with reference to hydroxyl ion concentration confirms that the hydrolysis takes place in steps as shown in the above equations (9)-(12), and not in a single step as in equation (13).

$$[Fe(CN)_6]^{3-} + 3OH^- \rightarrow Fe(OH)_3 + 6CN^- \quad (13)$$

Thus, it is clear from equations (9)-(12), the reaction (9) is most likely to be the rate-determining step, since the first attack of the hydroxyl is on the octahedral structure distorting the symmetry. Once the first CN^- is replaced, the further reaction proceeds fast and finally resulting in ferric hydroxide or hydrated ferric oxide.

Conclusion : It appears that there is a threshold concentration for the reaction between potassium hexacyanoferrate(III) and hydroxyl ion to take place evolving oxygen. This threshold concentration

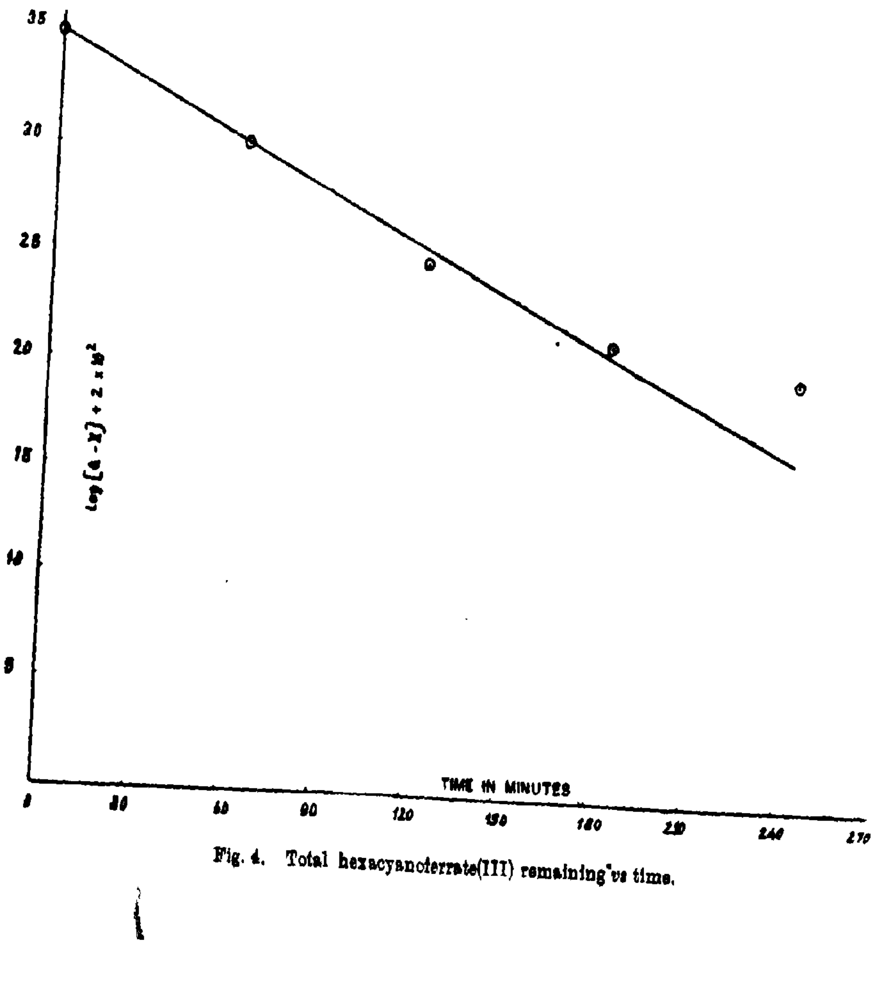


Fig. 4. Total hexacyanoferrate(III) remaining *vs* time.

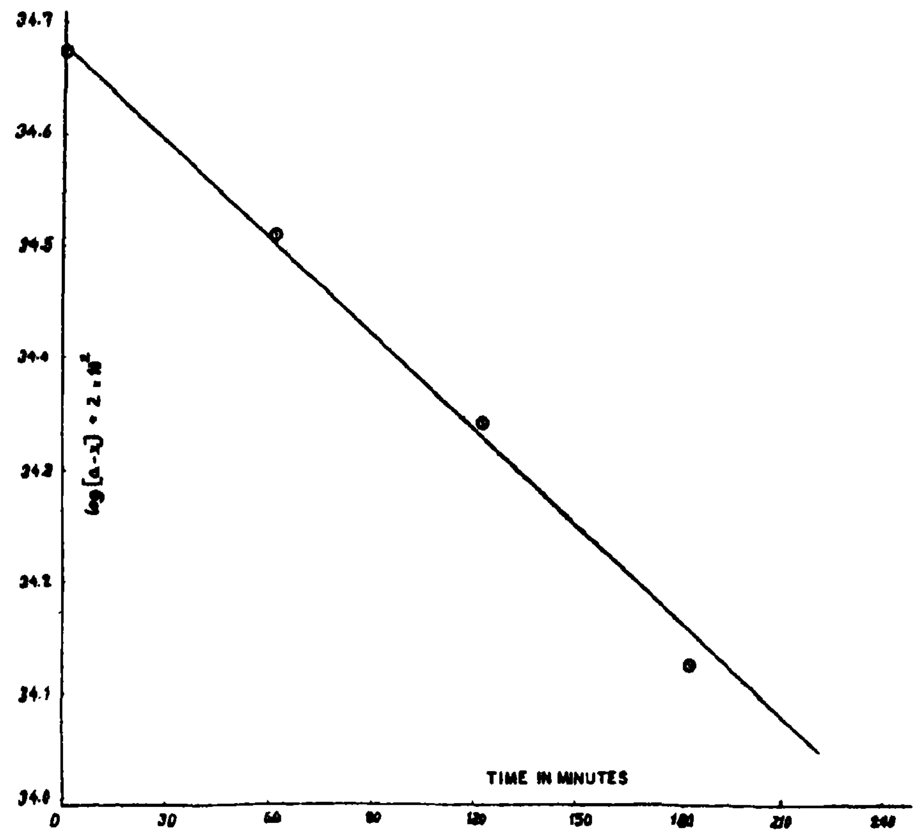


Fig. 5. Hexacyanoferrate(III) consumed for oxygen evolution vs time.

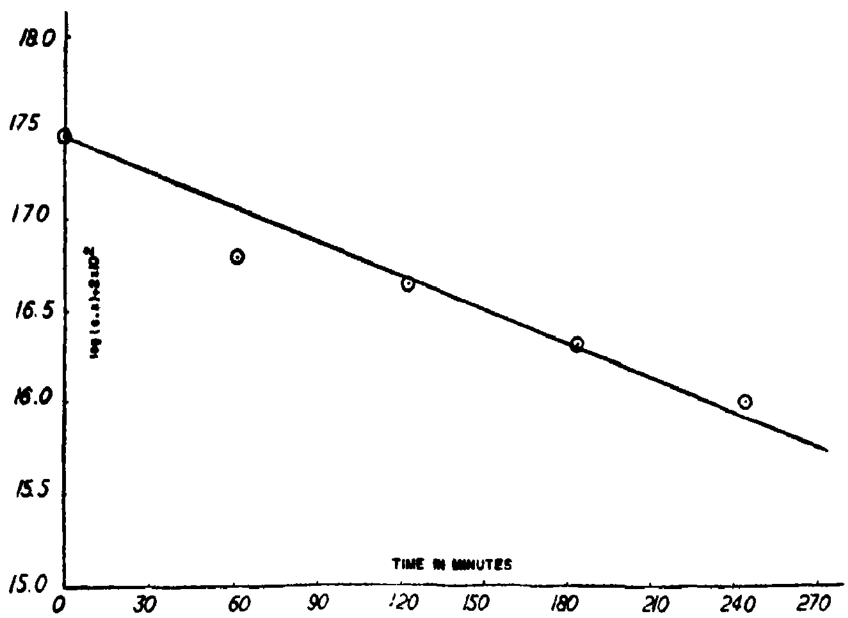


Fig. 6. Total OH ion concentration remaining vs time.

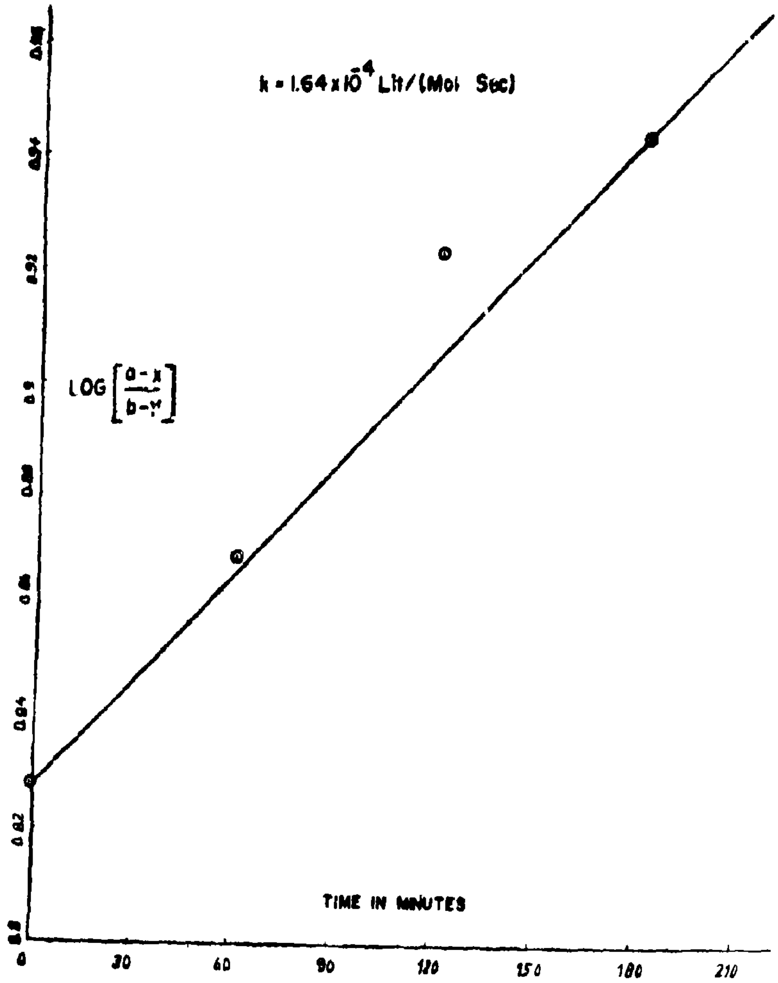


Fig. 7. Log $\left[\frac{a-x}{b-x}\right]$ vs time.

could be limited by applying a known potential to alkaline solutions. Efforts are presently in progress to identify the parameters that define the threshold concentration at the reaction zone.

Acknowledgement

The authors thank the referee for his suggestions.

References

1. D. P. MELLOR, "Modern Inorganic Chemistry", Longmans Green, London, 1961, p. 936.
2. EDWARD BARNES, *J. Indian Chem. Soc.*, 1939, **16**, 308.
3. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longmans, London, 1969, p. 371.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 757-759

Studies on Acid Dissociation Equilibria of 2-[(1*H*-Benzimidazol-2-ylmethylene)amino]benzoic Acid in Various Aquo-organic Media

K. L. OMPRAKASH, A. V. CHANDRA PAL and M. L. N. REDDY*

Department of Chemistry, Osmania University, Hyderabad-500 007

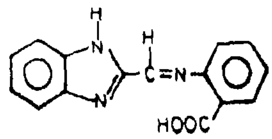
Manuscript received 10 June 1983, revised 4 April 1983, accepted 10 August 1984

A new Schiff base, 2-[(1*H*-benzimidazol-2-ylmethylene)amino]benzoic acid has been synthesised and characterised by spectral and analytical data. The acid dissociation constants of the Schiff base have been determined pH-metrically using the Irving-Rossotti titration technique. The influence of ionic strength, temperature and solvent on the acid dissociation equilibria of COOH and $\overset{+}{N}H$ groups has been studied. A comparison of ΔH and ΔS in different aquo-organic media reveals that the positive ΔS is the main driving force in the acid dissociation processes of these groups. The effect of solvent was discussed in the light of solute-solvent interactions in various aquo-organic mixtures.

SOLVENT effect on the *p*Ka values of a number of oxygenated acids (HA), like hydroxylic and carboxylic acids[1-3] showed a linear relationship with mole-fraction of the organic solvent. Conversely, nitrogenous[4,5] bases (cationic acids, BH^+), like anilines, pyridines and amines showed a reverse trend. Thus, in passing from water to high percentage of organic solvent, the strengths of the former acids become weaker while those of the latter stronger. Analogous trends were observed with the effect of ionic strength on these groups[6]. However, little work is reported on the effect of solvent and ionic strength on the acid dissociation reactions of the compounds that contain both these groups, and also on the synergistic behaviour of these groups. These studies are of interest in correlating the acid strengths in different solvent media. As benzimidazoles and Schiff bases are becoming increasingly important as biochemical, analytical and antimicrobial reagents, the Schiff base, 2-[(1*H*-benzimidazol-2-ylmethylene)-amino] benzoic acid [BMABA] was chosen for this purpose.

Experimental

The Schiff base, BMABA was prepared by refluxing (6 h) equimolar quantities (2 mmol) of benzimidazol-2-carboxaldehyde and anthranilic acid in ethanol (150 ml) containing 1 g sodium acetate. Pale yellow crystals separated on cooling in ice were filtered, washed with aqueous ethanol (5%) and repeatedly crystallised from ethanol to get a tlc pure product, m.p. 182° (Found: C, 67.02; H, 4.35; N, 15.55. $C_{15}H_{11}N_3O_2$ requires C, 67.83; H, 4.15: N, 15.85%). ν_{max} (KBr) 3250 br (NH), 2550-2700 (OH), 1690 (C=O), 1630 and 1600 cm^{-1} (C=N); δ (60 MHz; $CDCl_3$; TMS internal reference) 8.0 (s, 1H, HC=N), 7.45 (m, 8H, ArH). Based on the above data, structure I was assigned to the Schiff base.



I

The acid dissociation constants were determined using the Irving-Rossotti *p*H-titration technique[7], (i) at 20, 25, 30 and 40 in 50% and 70% v/v aq. dioxane, (ii) at I=0.03, 0.05, 0.10, 0.15 *M* ($NaClO_4$) in 50% v/v aq. dioxane at 30°, (iii) in 40, 50, 60 and 70% v/v aq. dioxane at 30°, and (iv) in 70% v/v aq. ethanol, aq. methanol, aq. isopropanol and aq. acetone at 30. The experimental details were those described earlier[9,10]. The calorimetric measurements were made adopting the reported procedures[11,12].

Results and Discussion

In the acid region, the ligand titration curve lies above the acid curve due to the basic property of the ligand nitrogens to accept protons from strongly acidic medium. However, in the basic region, it lies below the acid curve due to the release of COOH protons and hence the number of dissociable protons in the neutral molecule is one.

From the *p*H-titration curves, the values of $\bar{n}_H$ were evaluated using Irving-Rossotti method[7]. Proton-ligand formation curves were obtained by plotting *p*H *vs* $\bar{n}_H$. From these curves ($0.13 < \bar{n}_H < 1.96$), the values of pKa_1, and pKa_2 were evaluated by various computational techniques[8] and the values

were in agreement with each other. The standard deviations are within ± 0.01 pKa units.

The values of pKa_1 correspond to the proton of the tertiary nitrogen (pyridyl group) of the benzimidazole ring[9,10] and those of pKa_2 correspond to the proton of the COOH group. Dissociation of the imino proton of the imidazole ring was not observed even after pH 12.8. It was observed that the pK_{NH} values in 2-[(1*H*-benzimidazol-2-ylmethylene)amino]-phenol [BMAP][9] is higher when compared to BMABA. This may be due to the base strengthening mesomeric effect of phenolic-OH in BMAP. Conversely, in BMABA, the COOH group exerts a base weakening inductive (−I) effect on the other groups of the molecule. As a consequence, the basicity of azomethine nitrogen is lowered to such an extent ($pKa < 1.5$) that practically it showed no uptake of protons even from highly acidic medium.

Effect of ionic strength : A perusal of the data (Table 1) indicates that the values of pK_{COOH} decrease while pK_{NH} increase on increasing ionic strength. This is in conformity with the observations made on typical weak acids and bases (cationic acids), respectively[5,6]. In an acid dissociation reaction, the COOH group produces a negatively charged species from a neutral molecule while a basic group like $\overset{+}{N}H$ produces a neutral molecule from a positively charged (cationic) species. Thus, it can be concluded that

$$HL \xrightarrow{pK_{COOH}} H^+ + L^-$$

$$H_2L^+ \overset{pK_{NH}}{\rightleftharpoons} H^+ + HL$$

the molecule tends to remain in ionic form in a medium of high ionic strength. Linear plots were observed between $\sqrt{I}$ and either pK_{NH} or pK_{COOH}.

Effect of temperature : It was observed that the pK_{COOH} and pK_{NH} values decrease (Table 1) with an increase in temperature, suggesting that the dissociation reactions are favourable at higher temperatures. The thermodynamic parameters, *viz.* ΔG, ΔH and ΔS associated with the proton dissociation reactions were calculated utilizing the standard equations and are presented in Table 2. The ΔH values were also evaluated from simple calorimetric measurements and are consistant with those obtained from pH-metric data. The positive values of ΔG suggest that the proton dissociation reactions are not spontaneous. Further, the positive enthalpy change showed the endothermic nature of these reactions. Further, the ΔH values are almost constant in both 50% and 70% (v/v) aqueous dioxane. This is expected because the strength of the proton-ligand bond is essentially the same in both of these media. A comparison of the ΔH and ΔS terms in 50% and 70% (v/v) aqueous dioxane reveals that it is the positive entropy change which is the main driving force in these dissociation processes. Therefore, the difference in pKa values must be an entropy effect due to varying degree of solvation in different aquo-organic media.

Table 1—Acid Dissociation Constants of BMABA

Solvent = 50% v/v aq. dioxane

Temp. °C	I($NaClO_4$) *M*	pK_{COOH}	pK_{NH}
20	0.1	7.15	3.99
25	0.1	6.90	3.88
	0.00	6.95	3.42
	0.03	6.71	3.63
30	0.05	6.63	3.68
	0.10	6.56	3.72
	0.15	6.50	3.76
40	0.10	5.98	3.46

Temp = 30°, I = 0.10 *M* $NaClO_4$

Solvent %v/v	$1/\epsilon \times 10^2$	pK_{COOH}	pK_{NH}
40 D-W	2.427	6.35	3.71
50 D-W	3.053	6.56	3.72
60 D-W	4.082	6.87	3.66
70 D-W	5.814	7.22	3.60
70 A-W	2.649	7.03	4.02
70 M-W	2.165	6.51	4.15
70 E-W	2.517	6.67	3.94
70 I-W	3.195	6.81	3.89

D = dioxane, A = acetone, M = methanol, I = isopropanol, W = water.

Table 2—Thermodynamic Parameters Associated with Acid Dissociation Equilibria of BMABA

	Dioxane % v/v	pK_{COOH}	pK_{NH}
ΔG (30°)	50	38.07	21.69
kJ mol^{-1}	70	41.88	20.88
ΔH	50	104.48	47.82
kJ mol^{-1}	70	104.98	48.24
ΔS	50	219.24	86.65
J mol^{-1} deg^{-1}	70	207.19	91.00

Effect of solvent : The pK_{COOH} values increase with an increase in the dioxane content of the solvent mixture. Plot of pK_{COOH} *vs* mole-fraction (X_2) of dioxane was linear while that against $1/\epsilon$ showed a curvature. However, the initial points invariably fell on a straight line while the latter points, corresponding to low dielectric constant, deviated from it. Similar observations were made on a number of carboxylic acids[5,12]. This may be due to non-electrostatic forces that come into operation in the media of high organic content, where a change in the structuredness of the solvent occurs[13].

Solvent composition has little influence on the acid dissociation equilibria of the pyridyl ($\overset{+}{N}H$) group. On passing from 40% to 70% v/v dioxane, it becomes 0.11 pKa unit stronger. No linear plots were obtained between pK_{NH} and either X_2 or $1/\epsilon$. Similar observations were made with the acid dissociation equilibria of a number of cationic acids like anilines[4] and pyridines[5]. Such a reversal of the solvent effect on the pK_{NH} values when compared to pK_{COOH} may be due to the following solute-solvent interactions[14] in mixed-solvent systems. An

increase in the organic content of the solvent system results in a decrease in the dielectric constant of the medium. This will increase the electrostatic (ion-ion) interaction between a proton and a negatively charged oxygen atom to a greater extent than the ion-dipole interaction between the proton and the solvent. Thus, as dielectric constant decreases, the value of pKa increases for proton-ligand system containing O–H bonds. Conversely, an increase in the organic content of the solvent would be expected to increase the ion-dipole forces between a proton and a N-atom in the ligand to a lesser extent than the ion-dipole forces between a proton and the more electro-negative O-atom of the solvent. Therefore, a decrease in the value of pK_{NH} would be expected for compounds containing N–H bonds.

In 70% v/v mixed solvents, the pK_{COOH} values are in the order, dioxane > acetone > isopropanol > ethanol > methanol.

However, in the case of pK_{NH} values, the order is dioxane < isopropanol < ethanol < acetone < methanol. Except the position of acetone-water system, this is in conformity with the sequence of $1/\epsilon$ in these mixed solvents. The reversal of the position of acetone system may be due to its smaller proton solvation.

The degree of formation (α) of different protonated and non-protonated species as a function of pH was calculated using the expressions[1-8]

$$\alpha_{A^-} = \frac{1}{1+[H^+]/K_{COOH}+[H^+]^2/K_{NH}.K_{COOH}} \quad (1)$$

$$\alpha_{HA} = \frac{[H^+]/K_{COOH}}{1+[H^+]/K_{COOH}+[H^+]^2/K_{NH}.K_{COOH}} \quad (2)$$

$$\alpha_{H_2A^+} = \frac{[H^+]^2/K_{NH}.K_{COOH}}{1+[H^+]/K_{COOH}+[H^+]^2/K_{NH}.K_{COOH}} \quad (3)$$

The same were graphically represented as distribution diagrams (Fig. 1). It can be seen that the proportions of H_2A^+ and A^- change monotonically with pH, whereas the intermediate species, HA attains a certain maximum. Thus, H_2A^+ exists upto pH 5.0, HA between pH 2.5 to 7.5, and A^- above pH 5.5 in significant proportions.

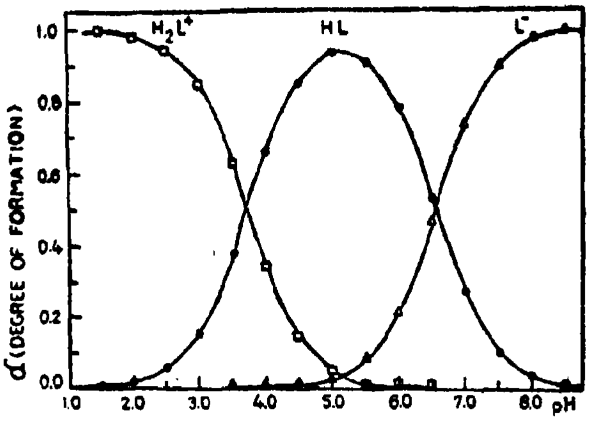


Fig. 1. Distribution diagram for BMABA.

Acknowledgement

The authors are grateful to the C.S.I.R., New Delhi for the award of a Post-Doctoral Fellowship to one of them (K.L.O.P.).

References

1 H. Irving and H. Rossotti, *Acta Chem. Scand.*, 1956, **10**, 72.
2. D. N. Shelke and D. V. Jahagirdar, *J. Indian Chem. Soc.*, 1978, **55**, 545.
3. A. K. Chaudhury, N. Kole and S. P. Ghosh, *J. Indian Chem. Soc.*, 1981, **58**, 248.
4. E. Grunwald and B. Gutbrzahal, *J. Am. Chem. Soc.*, 1953, **75**, 559.
5. T. R. Harkins and H. Freiser, *J. Am. Chem. Soc.*, 1955, **77**, 1374.
6. G. I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, 1962, 2745.
7. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904.
8. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397.
9. K. L. Omprakash, A. V. Chandra Pal and M. L. N. Reddy, *Indian J. Chem., Sect. A*, 1982, **21**, 322.
10. K. L. Omprakash, A. V. Chandra Pal and M. L. N. Reddy, *Natl. Acad. Sci. Lett.*, 1981, **4**, 407.
11. H. Freiser and D. Fleischer, *J. Phys. Chem.*, 1959, **63**, 260.
12. S. C. Lahiri, A. K. Roy and S. Aditya, *Thermochim. Acta*, 1976, **16**, 277.
13. H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 1945, **13**, 507, 363.
14. R. P. Bell and A. F. Dickenson, *J. Chem. Soc.*, 1949, 1288, 1293.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 760-764

Effect of Compaction on Kinetics of Thermal Dehydration of Silicic Acid and Aluminium Hydroxide Hydrogels

N. K. MITRA, S. SINHAMAHAPATRA and A. BASUMAJUMDAR

Department of Chemical Technology, University of Calcutta, Calcutta-700 009

Manuscript received 17 February 1984, accepted 10 August 1984

The dehydration kinetics have been studied by TG method. The effect of compaction could not contribute to major changes in the hydrogel structures and also in the orientation of water molecules. Effect of increase of pressure was inversely affecting the validity of first order kinetics. The escape of loosely bound water was a low-energy process.

WATER is an integral part of the gel structure. Various physico-chemical properties of the hydrogels depend on the magnitude and orientation of water molecules. Thus water is thought to be the solely decomposition product of hydrous oxides. This can either be formed uniformly throughout the crystal by combination of hydroxyl group with the proton of an adjacent group (homogeneous mechanism) or by a countermigration of protons and metal ions to region which subsequently forms water and oxide, respectively (inhomogeneous mechanism).

Gelatinous aluminium hydroxide materials are of great interest because of their industrial importance in preparing sorbents and catalysts. Various types of gels were investigated[1-3], in most cases precipitated from alum or aluminium sulfate solution by ammonia at a temperature below 60°. Alumina-gels were prepared[4] at pH 3.5 to 7.0. Kendykin[5] stated that primary amorphous particles are oval, 0.01 to 0.05 micron in diameter, in agreement with the size as determined from specific surface measurements.

Jingensons and Straumanis[6] were the first to study thoroughly the release and uptake of liquids by rigid, irrerversible gels of silicic acid, ferric hydroxide and aluminium hydroxide. Silicic acid hydrogel is used only to designate the harder, partially or entirely dehydrated product. Silicic acid hydrogel which is normally prepared by the destabilisation of an aqueous solution of sodium silicate has been used since long as a dehydrating agent in various processes.

The surface properties of the silicic acid hydrogel were shown to be independent of the crystalline state. Silicic acid hydrogels in various thermal treatments were studied by glc method[8] and their changes in pore size, inner surface and structural water content worked out. An extensive review of kinetic processes involving solids has been made[9] and reactions were classified into the categories of exothermic and endothermic types. It was shown[10] that the rate of decomposition was influenced by grain size and the attendant surface area. It was found[11] that the rate-constant during zeolitic dehydration followed an inverse relationship with the total water content. The activation energy was shown to be independent of particle size in aluminosilicate gel structure[12].

The present investigation reports the effect of compaction on the kinetics of thermal dehydration of two important hydroxide hydrogels.

Experimental

Silicic acid hydrogel was synthesised by cation exchange technique. After proper ageing, they were processed in accordance with the reported method[13], in order to get rid of extraneous impurities. Aluminium hydroxide hydrogel was prepared by the interaction of $Al_2(SO_4)_3.18H_2O$ and NH_4Cl-NH_4OH buffer at pH 9. Finally, the materials were processed with the reported method[14]. The kinetics of dehydration process was studied by TG method[15]. Pellets were prepared in hydraulic press by taking 0.5 g finely agated powder at the pressure of 1150, 1350 and 1550 kg/cm^2 for 1 min. No binder was used and the pellets were sufficiently strong. After fabrication, the pellets were equilibrated at 32±1°.

Results and Discussion

The isothermal dehydration curves (not produced) showed exponential behaviour and as such first order kinetics was suggested. The method of Guggenheim[16] was adopted to calculate initial water concentration (L_a) which can be dehydrated at the experimental temperature and also the rate constant K_1 for the initial stage of dehydration using equation (1).

$$\log \Delta L = \frac{-K_1 t}{2.303} + \log L_a[1 - \exp(-K_1 \Delta t)] \qquad (1)$$

where ΔL is the difference between the mass loss at time $(t+\Delta t)$ and time t, the time interval Δt between the two sets of readings being kept fixed at a value greater than twice the time for 50% dehydration. Using equation (1), the rate constant was calculated from the slope of linear plots obtained by plotting log ΔL *vs* t. Knowing t and having obtained K_1 from the slope, L_α was determined from the intercept on the log axis. Figs. 1 to 6 show the Guggenheim plots and the values of K_1 and L_α are recorded in Table 1. The activation energy was calculated from the usual Arrhenius plots using the rate constants (Figs. 7 and 8).

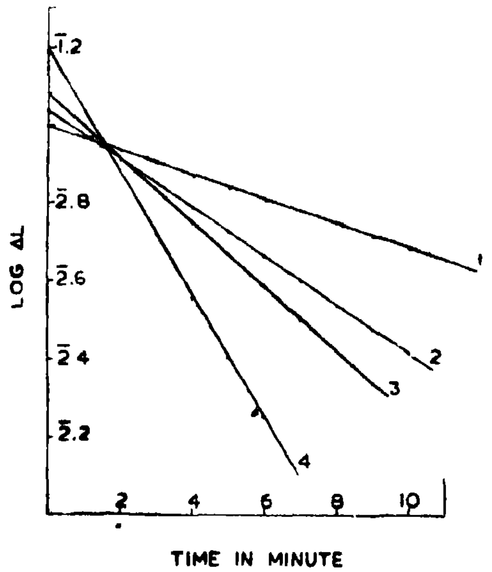


Fig. 1. Log ΔL *vs* time plots of silicic acid hydrogel pelletised under 1150 kg/cm² pressure at different temperatures : (1) 100°, (2) 130°, (3) 160°, (4) 190°.

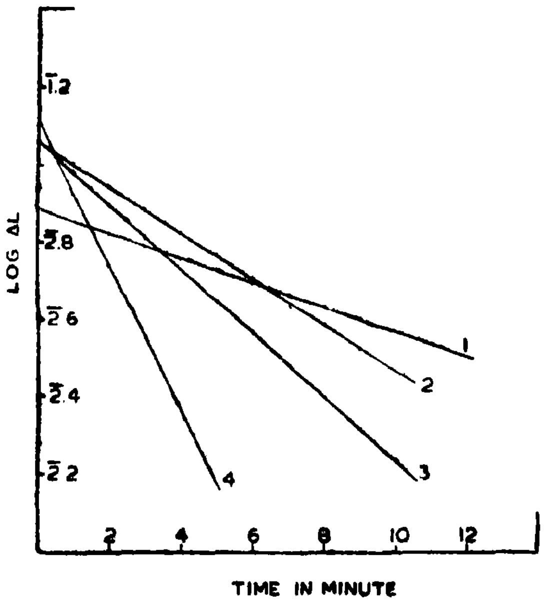


Fig. 2. Log ΔL *vs* time plots of silicic acid hydrogel pelletised under 1350 kg/cm² pressure at different temperatures : (1) 100°, (2) 130°, (3) 160°, (4) 190°.

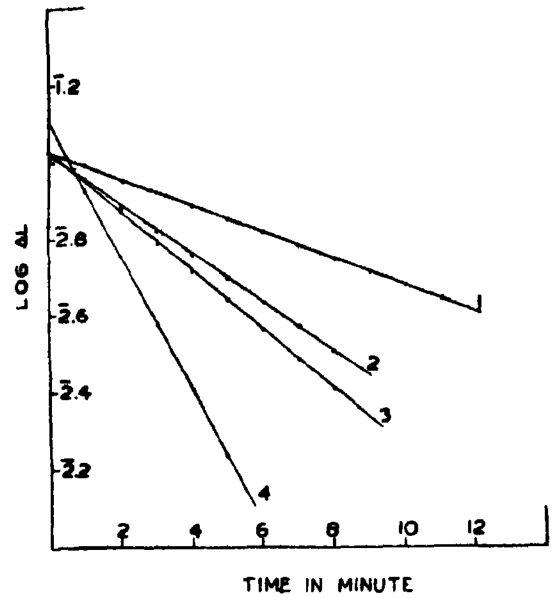


Fig. 3. Log ΔL *vs* time plots of silicic acid hydrogel pelletised under 1550 kg/cm² pressure at different temperatures : (1) 100°, (2) 130°, (3) 160°, (4) 190°.

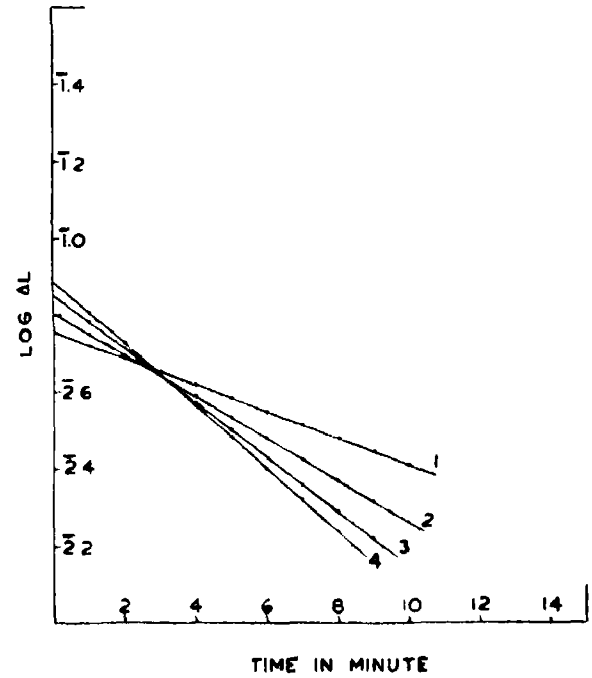


Fig. 4. Log ΔL *vs* time plots of aluminium hydroxide hydrogel pelletised under 1150 kg/cm² pressure at different temperatures : (1) 100°, (2) 130°, (3) 160°, (4) 190°.

From an analysis of the above results, it has been found that at a given temperature the L_α values for the three different pressures (1150-1550 kg/cm²) of pelletisation, remain almost the same and this was also expected since any variation in pressure might alter the rate of dehydration but not the final loss at infinite time.

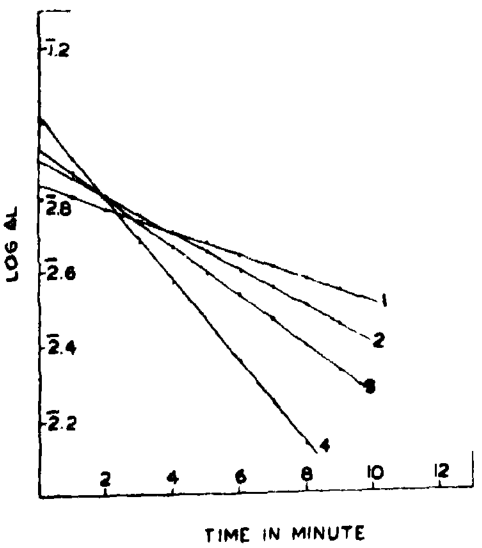


Fig. 5. Log ΔL *vs* time plots of aluminium hydroxide hydrogel pelletised under 1350 kg/cm² pressure at different temperatures : (1) 100°, (2) 130°, (3) 160°, (4) 190°.

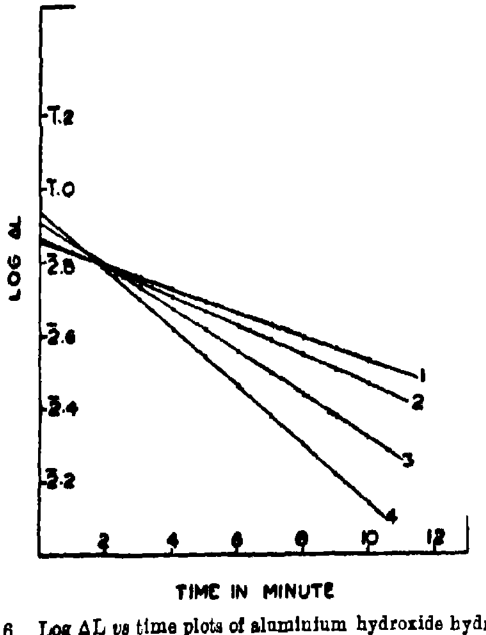


Fig. 6. Log ΔL *vs* time plots of aluminium hydroxide hydrogel pelletised under 1550 kg/cm² pressure at different temperatures : (1) 100°, (2) 130°, (3) 160°, (4) 190°.

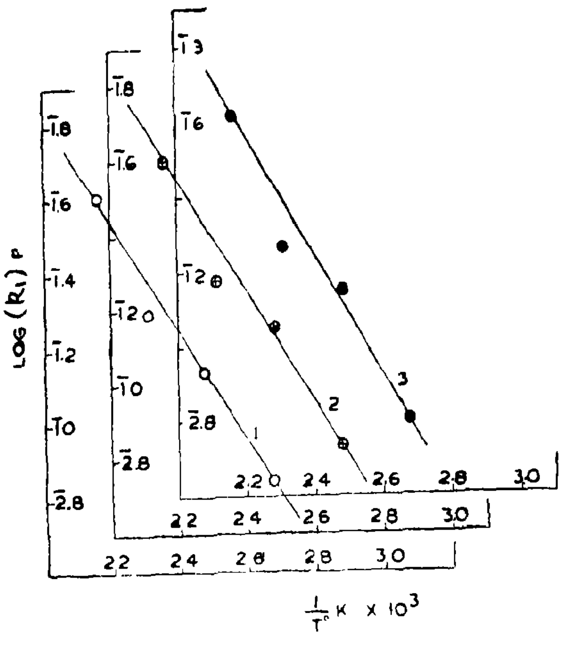


Fig. 7. Arrhenius plots of pellets of silicic acid hydrogel compacted under different pressure for the initial stage of dehydration : (1) 1150, (2) 1350, (3) 1550 kg/cm².

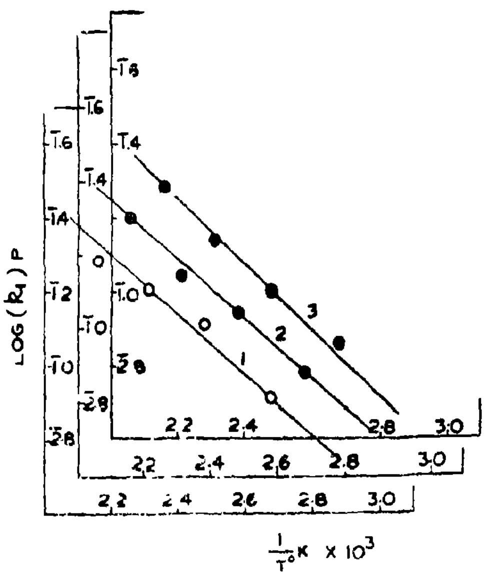


Fig. 8. Arrhenius plots of pellets of aluminium hydroxide hydrogel compacted under different pressure for the initial stage of dehydration : (1) 1150, (2) 1350, (3) 1550 kg/cm².

The rate constants of dehydration for both of silicic acid and aluminium hydroxide hydrogel, were found to be reduced on application of pressure which might be due to the back pressure set up by water vapour in the pores. In the study of pressure-effect the reaction rate constants were calculated only for the initial stage of dehydration. In the pressurised condition, the rate of dehydration decreased in comparison to that of loose grains.

No significant pressure effect was observed with respect to the $(Kp)_1$ values in the range studied in the present investigation which might be due to the fact that no overall compaction, particle disintegration or orientation occurred. Thus it appears that there might be a critical pressure upto which reaction rate may decrease (not studied here) but beyond that point the change was not very significant.

TABLE 1—VALUES OF RATE CONSTANTS $(Kp)_1$ AND L_∞ AS DETERMINED FROM LOG ΔL *vs* TIME PLOTS AT DIFFERENT PRESSURES AT THE INITIAL STAGE OF DEHYDRATION

Hydrogel	Temp. °C	Pressure of pelletisation kg/cm²	$(Kp)_1$/min	L_∞ g
Silicic acid	100	1150	0.0690	0.1142
		1350	0.0678	0.1156
		1550	0.0686	0.1146
Silicic acid	130	1150	0.1898	0.1238
		1350	0.1888	0.1232
		1550	0.1890	0.1280
Silicic acid	160	1150	0.1892	0.1252
		1350	0.1886	0.1255
		1550	0.1842	0.1260
Silicic acid	190	1150	0.4062	0.1264
		1350	0.3998	0.1260
		1550	0.4030	0.1278
Aluminium hydroxide	100	1150	0.0806	0.0340
		1350	0.0751	0.0332
		1550	0.0721	0.0336
Aluminium hydroxide	130	1150	0.1290	0.0448
		1350	0.1092	0.0520
		1550	0.1004	0.0526
Aluminium hydroxide	160	1150	0.1578	0.0560
		1350	0.1382	0.0580
		1550	0.1374	0.0575
Aluminium hydroxide	190	1150	0.1890	0.0595
		1350	0.1886	0.0586
		1550	0.1879	0.0590

From the extent of linearity of log $[(L_\infty\text{-}L)/L_\infty]$ *vs* time plots (Figs. 9-12), the validity of first order law was examined with respect to variation of pressure and the results are given in Table 2.

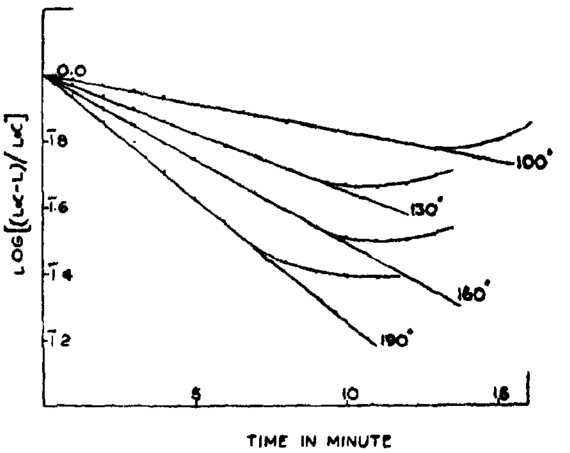
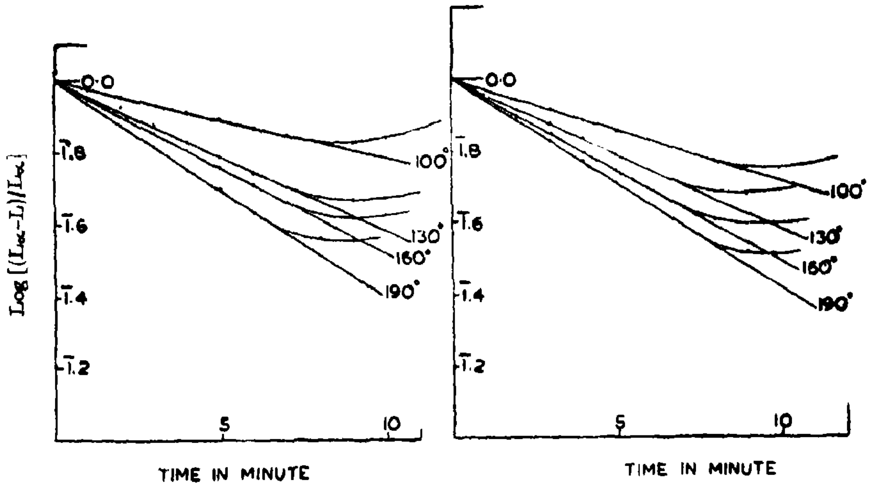


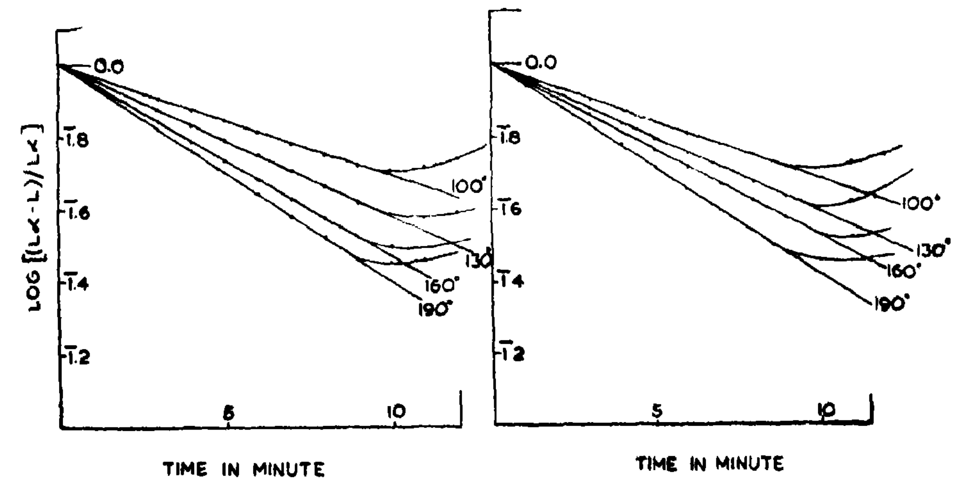
Fig. 9. Isothermal dehydration curve for silicic acid hydrogel pelletised under 1150 kg/cm² pressure at different temperatures.



Pressure, 1550 kg/cm²

Pressure, 1350 kg/cm²

Fig. 10. Isothermal dehydration curves of silicic acid hydrogel pelletised under different pressures.



Pressure, 1150 kg/cm²

Pressure, 1350 kg/cm²

Fig. 11. Isothermal dehydration curves for aluminium hydroxide hydrogel pelletised under different pressures at different temperatures.

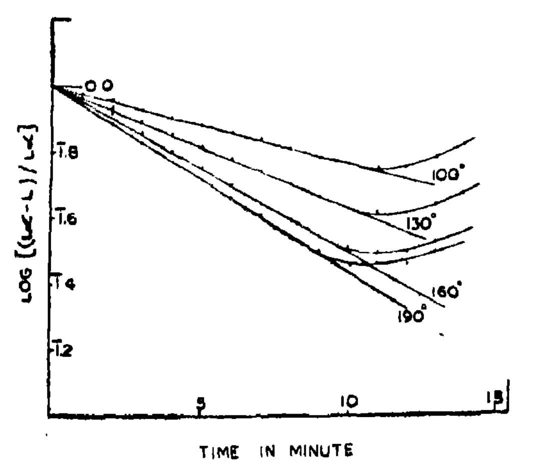


Fig. 12. Isothermal dehydration curves for aluminium hydroxide hydrogel pelletised under 1550 kg/cm² pressure at different temperatures.

TABLE 2—EXTENT OF VALIDITY OF FIRST ORDER LAW AS DETERMINED FROM log $[(L_\infty - L)/L_\infty]$ *vs* TIME PLOTS

Hydrogel	Temp. °C	Pressure of pelletisation kg/cm²	First order valid upto % dehydration
Silicic acid	100	1150	41.16
		1350	39.74
		1550	32.39
Silicic acid	130	1150	52.14
		1350	49.88
		1550	48.71
Silicic acid	160	1150	66.21
		1350	56.35
		1550	52.02
Silicic acid	190	1150	69.80
		1350	65.83
		1550	61.10
Aluminium hydroxide	100	1150	48.72
		1350	47.62
		1550	45.05
Aluminium hydroxide	130	1150	61.19
		1350	60.09
		1550	58.32
Aluminium hydroxide	160	1150	67.56
		1350	66.89
		1550	66.38
Aluminium hydroxide	190	1150	71.16
		1350	69.80
		1550	69.10

Effect of pressure was noticed in the validity of the first order kinetics which was inversely affected by the increase of pressure. This might be due to the fact that under pressurised condition the escape of water is retarded through the compact mass containing decomposed materials whose surfaces were still hydrophilic in nature. The calculated values of activation energy from Arrhenius plot have been represented in Table 3 and Figs. 7 and 8.

In each case activation energy increased and showed a positive proportionality with the pressure of pelletisation. The escape of loosely bound water

TABLE 3—ACTIVATION ENERGIES AS DETERMINED FROM ARRHENIUS PLOTS AT THE INITIAL STAGE OF DEHYDRATION OF HYDROXIDE HYDROGEL FORMED AT DIFFERENT PRESSURE

Hydrogel	Pressure of pelletisation kg/cm²	Activation energies $(Ep)_i$ cal mol⁻¹
Silicic acid	1150	6.64
	1350	6.86
	1550	7.32
Aluminium hydroxide	1150	3.75
	1350	3.89
	1550	4.12

was a low energy process as evidenced from the values of activation energy and as such the variation with respect to pressure was fairly significant. Although under pressurised condition there is possibility of particle disintegration along with formation of channels yet no such effect was noticed within the pressure range as studied in the present investigation.

Conclusion : (i) Positive effect of pressure was noticed in the validity of the first order kinetics which was inversely affected by the increase of pressure.

(ii) Rate constants of the initial stage of dehydration decreased in comparison to that of loose grains which might be due to the back pressure set up by the water vapour inside the pore.

(iii) Under pressurised condition only the exposed surface area was diminished. But because of the highly porous hydrogel, no positive extra diffusion barrier was created due to compaction and as such the pressure effect was not very significant.

References

1. R. WILLSTATTER and H. KRANT, *Chem. Ber.*, 1923, **56**, 149.
2. R. WILLSTATTER and H. KRANT, *Chem. Ber.*, 1923, **56B**, 1117.
3. R. WILLSTATTER, H. KRANT and O. ERABACHER, *Chem. Ber.*, 1925, **58**, 2448.
4. R. H. CRAMER and E. E. JENKINS, U. S. 2 898 306/1959
5. Y. U. M. KENDYKIN, *Kolloidn. Zh.*, 1964, **26**, 318.
6. B. JINGERSONS and M. E. STRAUMANIS, "Text Book of Colloid Chemistry", 2nd. ed., Paragon Press, 1962, p. 398.
7. T. TAKAMURA, *Kolloid. Z.*, 1958, **157**, 11.
8. F. WOLF and H. BAYER, *Z. Anorg. Allg. Chem.*, 1959, **300**, 33.
9. W. E. GARNER, "Chemistry of the Solid State". Butterworth, London, 1955, pp. 213-32.
10. G. H. WHITING and W. E. S. TURNER, *J. Soc. Glass Technol.*, 1930, **14**, 409.
11. N. K. MITRA, S. GHATAK and S. MITRA, *Indian J. Chem., Sect. A*, 1980, **19**, 195.
12. N. K. MITRA, K. L. ROY and S. MITRA, *Trans. Brit. Ceram. Soc.*, 1975, **74**, 263.
13. N. K. MITRA, S. C. DE, A. CHATTERJEE and S. SINHAMAHAPATRA, *Indian Ceramics*, 1981, **23**, 235.
14. N. K. MITRA, S. SINHAMAHAPATRA and A. CHATTERJEE, *Indian Ceramics*, 1981, **24**, 27.
15. N. K. MITRA, K. L. ROY and S. MITRA, *Trans. Brit. Ceram. Soc.*, 1975, **74**, 263.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 765-769

Conductance Behaviour of Potassium and Silver Dodecyl Sulphates in Polar Solvents

P. BAHADUR* and (Miss) A. GUPTA

D. A. V. College, Muzaffarnagar

and

P. BAHADUR

Department of Chemistry, South Gujarat University, Surat-395 007

Manuscript received 18 January 1982, revised 6 September 1982, accepted 10 March 1983

The critical micelle concentrations of potassium and silver dodecyl sulphates in lower alcohols, alcohol-water and alcohol-benzene mixtures were determined conductometrically. The conductance data have been used to calculate the thermodynamic parameters of micellization.

CONDUCTANCE behaviour of metal dodecyl sulphates in aqueous medium has been studied by several workers[1-12]. However, data on their solution behaviour in alkanols are not reported. There has been a controversy in solution behaviour of surfactants in alkanols. Several authors suggest the presence of micelles[13-17] of surfactants in solutions in alkanols while some others have commented on absence of micelles[18,19]. In this paper we have examined the micellar behaviour of silver and potassium dodecyl sulphates in lower alkanols, alkanol-water and alkanol-benzene mixtures of varying compositions by conductivity method.

Experimental

Extra-pure sodium dodecyl sulphate was used for preparation of silver and potassium salts[11]. Reagent grade chemicals were used throughout the experiment. Conductivity water ($K \sim 1 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$) was taken. Conductance measurements were carried out using Philips conductivity bridge at constant temperature. The conductivity data were reproducible to 0.1%.

Results and Discussion

The CMC values of metal dodecyl sulphates in different alkanols (methanol, propan-1-ol, propan-2-ol and butan-1-ol) over the temperature range (35-50°) were determined from the intersection of two straight line portions of the specific conductance (K) *vs* concentration (C) plots (a representative set of curves is shown in Fig. 1) and are recorded in Tables 1 and 2. Studies on potassium dodecyl sulphate in propan-1-ol and propan-2-ol could not be carried out owing to its low solubility in these alkanols. The CMC values increase with increase in temperature but decrease with increasing carbon

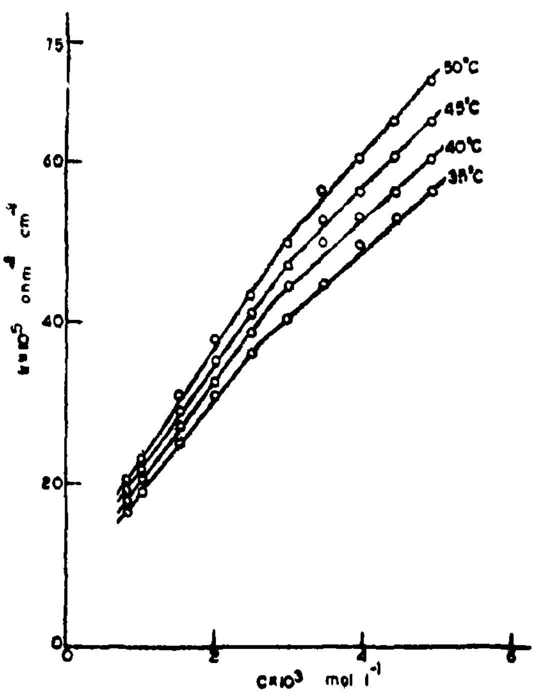


Fig. 1. Specific conductance *vs* concentration plots for silver dodecyl sulphate in propan-1-ol at different temperatures.

number in the alkanols used as solvent. The CMC values of potassium dodecyl sulphate were higher than those for silver dodecyl sulphate.

The aggregation of potassium dodecyl sulphate in methanol-water and methanol-benzene mixtures of different compositions was also studied and the CMC values obtained from K – C plots are recorded in Table 3. The CMC values were found independent of water concentration for methanol-water

TABLE 1—VALUES OF CMC, CONSTANTS AND THERMODYNAMIC PARAMETERS FOR METAL DODECYL SULPHATES IN POLAR SOLVENTS

Temperature 40°

System	CMC × 10^3 mol l^{-1}	A	B	λ_∞ Ω^{-1} cm^2 eq^{-1}	K × 10^4 Ω^{-1} cm^{-1}	$-\Delta G_D^0$ kcal	$-\Delta G_A^0$ kcal
			KDS				
Methanol	3.10	1.615	0.125	—	—	—	11.40
Butan-1-ol	2.20	1.550	0.400	12.00	6.25	4.59	10.86
			AgDS				
Methanol	3.00	$\bar{1}$.745	0.750	—	—	—	11.52
Propan-1-ol	2.80	0.330	0.330	34.90	9.02	4.36	10.82
Propan-2-ol	2.00	$\bar{1}$.970	0.400	27.50	3.90	4.88	11.24
Butan-1-ol	1.40	$\bar{1}$.870	0.400	—	—	—	11.42

mixtures and the identical values obtained were in between the CMC in water and methanol[20]. However, the CMC was found to decrease with increasing amount of benzene in methanol-benzene mixtures. The decreasing trend in CMC for methanol-benzene mixture has been depicted in Fig. 2. Such a decrease in CMC of surfactant with increasing benzene content in the solvent mixture appears due to the decreasing polar character of the solvent. Figs. 3 and 4 represent plots of the specific conductance *vs* volume % of additives in methanol. In Fig. 3 the conductance data seem to acquire a limiting value at 50% benzene. Conductivity of surfactant solution with higher volume % was not determined for physical in significance. However, Fig. 4 shows that the specific conductance initially decreases with the addition of water up to 40% and then increase with further addition. It may therefore be suggested that a change in the nature of solvent occurs at about 50% composition for both the solvents.

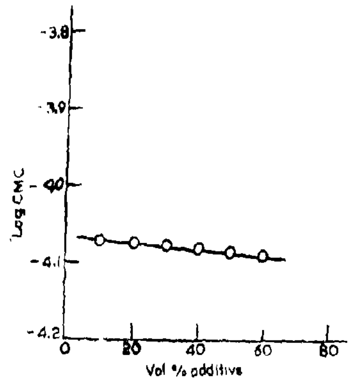


Fig. 2. Log CMC *vs* volume % benzene for potassium dodecyl sulphate in methanol-benzene mixture.

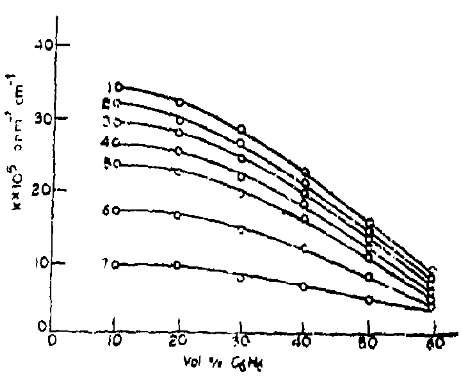


Fig. 3. Specific conductance *vs* volume % benzene for potassium dodecyl sulphate in methanol-benzene mixtures: (1) 0.0050, (2) 0.0045, (3) 0.0040, (4) 0.0035, (5) 0.0030, (6) 0.0020 and (7) 0.0010 mol l^{-1}.

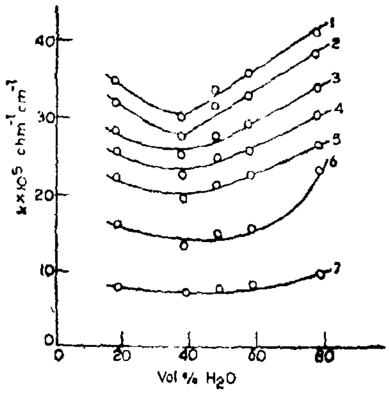


Fig. 4. Specific conductance *vs* volume % water for potassium dodecyl sulphate in methanol-water mixtures: (1) 0.0050, (2) 0.0045, (3) 0.0040, (4) 0.0035, (5) 0.0030, (6) 0.0020, (7) 0.0010 mol l^{-1}.

The conductance behaviour of both the surfactants in the system has been satisfactorily expressed by the equation[21]

$$\log \lambda = A + B \log C.$$

The values of constants A and B evaluated by extrapolating log λ *vs* log C plot (Fig. 5) are recorded in Tables 1-3. The values of constant A which signify limiting molar conductance have got theoretical importance, since it is not possible to prepare molar soap solutions owing to their low solubility. The trend in the change of constants A and B at 50% volume in solvent mixture is likely due to the changing nature of solvent which causes changes in the nature of micelles from alcomicelles to hy-

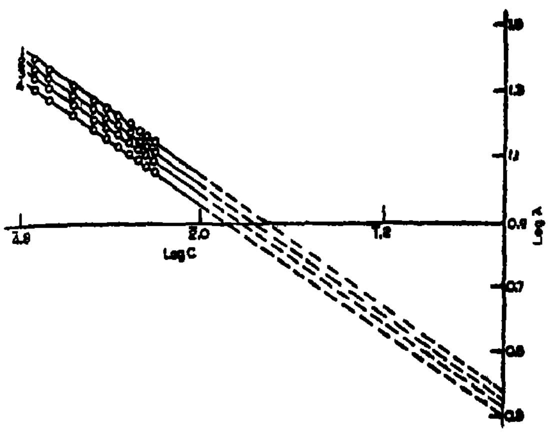


Fig. 5. Log molecular conductance *vs* log concentration for silver dodecyl sulphate in propan-1-ol : (1) 50°, (2) 45°, (3) 40° and (4) 35°.

dromicelles (in alkanol-water mixture), and alcomicelles to oleomicelles (in alkanol-benzene mixture). Such a change in behaviour of solvent has also been observed previously.

TABLE 2—VALUES OF CMC AND OTHER CONSTANTS FOR SILVER DODECYL SULPHATE IN PROPAN-1-OL

Temperature °C	CMC×10³ mol l⁻¹	A	B	λ_∞ Ω^{-1} cm² eq⁻¹	K×10⁴ Ω^{-1} cm⁻¹
35	2.60	0.300	0.325	31.90	9.56
40	2.80	0.330	0.330	34.90	9.02
45	3.00	0.350	0.335	36.90	8.80
50	3.20	0.380	0.340	41.60	7.98

Since these surfactants in alkanols behave like weak electrolytes, the expression for their dissociation can be derived[22].

$$MDS \rightleftharpoons M^{+} + DS^{-}$$

$$C(1-\alpha) \quad C\alpha \quad C\alpha$$

$$K = \frac{C\alpha^2}{(1-\alpha)}$$

Where α is the degree of dissociation and K the dissociation constant. Since α in such systems i very small, interionic effects may be treated a negligible. Thus considering α as λ_M/λ_∞ :

$$C\lambda_M = \frac{K\lambda_\infty^2}{\lambda_M} - K\lambda_\infty$$

The plots of $C\lambda_M$ *vs* $1/\lambda_M$ are linear (Fig. 6) below CMC except for methanol and methanol-benzene systems where the plots are not linear. However, the equation fails above the CMC as the process of

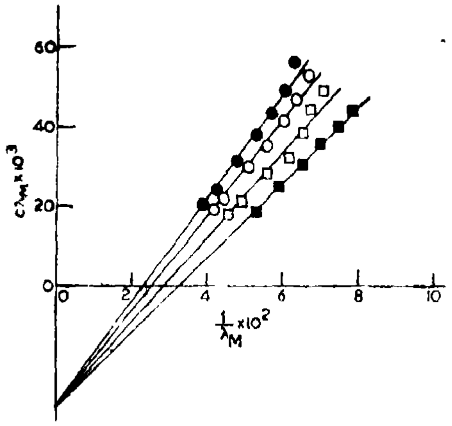


Fig. 6. $C\lambda_M$ *vs* $1/\lambda_M$ for silver dodecyl sulphate in propan-1-ol : ● 50°, ○ 45°, □ 40° and ■ 35°.

aggregation takes place. The dissociation constant (K) and the molar conductance at infinite dilution (λ_∞) for both the surfactants in different solvent systems were evaluated from the slopes and intercepts of the above plots and are recorded in Tables 1-3. Further, the heat of dissociation for silver dodecyl sulphate in propan-1-ol obtained from the linear slopes of log K *vs* 1/T plots (Fig. 7) is −2.28 kcal.

The free energy for the dissociation process, ΔG_D was evaluated from the expression[23,24]

$$\Delta G_D^0 = -RT \ln K_A$$

TABLE 3—VALUES OF CMC, CONSTANTS AND THERMODYNAMIC PARAMETERS FOR POTASSIUM DODECYL SULPHATE IN MIXTURES

Temperature 40°

System	CMC×10³ mol l⁻¹	A	B	λ_∞ Ω^{-1} cm² eq⁻¹	K×10⁴ Ω^{-1} cm⁻¹	$-\Delta G_D^0$ kcal	$-\Delta G_A^0$ kcal
Water in methanol							
20%	5.50	1.595	0.110	96.70	0.95	2.90	10.94
40%	5 50	1.545	0.100	80.00	0.93	2.91	11.10
50%	5.50	1.630	0.085	81.34	1.65	2.55	11.16
60%	5.50	1.670	0.075	86.00	1.74	2.52	11.24
80%	5.50	1.720	0.070	97.87	2.40	2.32	11.34
Benzene in methanol							
10%	2.500	1.460	0.170	—	—	—	11.66
20%	2.325	1.410	0.170	—	—	—	11.66
30%	2.175	1.350	0.170	—	—	—	11.66
40%	1.980	1.255	0.175	—	—	—	11.70
50%	1.825	0.880	0.260	—	—	—	11.70
60%	1.625	0.395	0.360	—	—	—	11.72

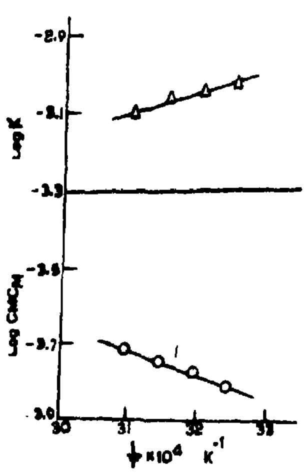


Fig. 7. Log K and log CMC$_M$ *vs* 1/T for silver dodecyl sulphate in propan-1-ol.

where K_A is the equilibrium constant for association process[23,24].

Again, $\Delta G_D^o = -RT \ln 1/K_D = RT \ln K_D$

Where K_D is the equilibrium constant for dissociation process, *i.e.* dissociation constant.

Now for aggregation process, when counter ions are bound to the micelle, the standard free energy of micellization (per mole of monomer), ΔG_A^o, for the phase separation model is given by the expression[25]

$$\Delta G_A^o = 2RT \ln CMC_M.$$

Where CMC_M is expressed as a mole fraction and where the total number of moles present at the CMC is equal to the sum of moles of solvent and surfactant. The free energies for the dissociation and micellization processes for the system are recorded in Tables 1-3.

Again, the standard enthalpy change of micellization (ΔH_A^o) per mole of monomer from the same approach[25] is given by

$$\frac{\delta}{\delta T} \cdot \ln CMC_M = \frac{\Delta H_A^o}{RT^2}$$

$$\text{or } \ln CMC_M = \frac{\Delta H_A^o}{RT} + C$$

ΔH_A^o for silver dodecyl sulphate in propan-1-ol has been calculated from the linear plot of log CMC_M *vs* 1/T (Fig. 7) and is +2.75 kcal. This value indicates that the net energy involved in the micellization process is greater than that involved for dissociation of surfactants. This is also in accordance with the free energy data for dissociation and micellization of surfactants in all other systems.

The standard entropy changes for dissociation and micellization processes ΔS_D^o and S_A^o for silver dodecyl sulphate in propan-1-ol were evaluated using the expression

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}.$$

ΔG^o and ΔS^o values for dissociation and micellization processes have been plotted against the temperature (Fig. 8). The $\Delta G_{A,D}^o$ values increase linearly with temperature and CMC_M (Fig. 9). On the other hand, a linear decrease/increase was seen in $\Delta S_A^o/\Delta S_D^o$ values. Furthermore, ΔS^o values for micellization process were also higher than the values of ΔS^o for dissociation.

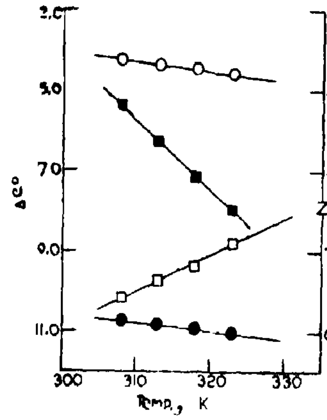


Fig. 8. Free energy (and entropy) *vs* temperature of silver dodecyl sulphate in propan-1-ol.
O ΔG_D, □ ΔS_D, ● ΔG_A and ■ ΔS_A.

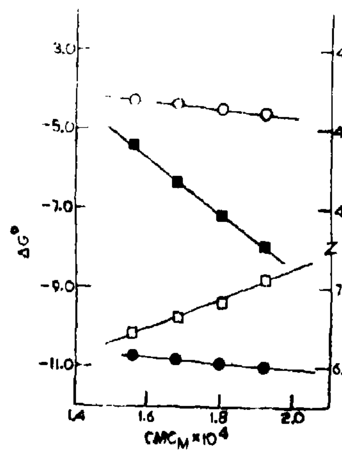


Fig. 9. Free energy (and entropy) *vs* CMC$_M$ of silver dodecyl sulphate in propan-1-ol :
O ΔG_D, □ ΔS_D, ● ΔG_A and ■ ΔS_A.

Acknowledgement

One of the authors (A.G.) gratefully acknowledges the award of fellowship from C.S.I.R., New Delhi. The authors are thankful to Dr. R. P. Varma and Dr. G. Singh for their valuable criticism and to college authorities for providing necessary facilities.

References

1. B. D. Flockhart and A. R. Ubbelohde, *J. Colloid Sci.*, 1953, **8**, 427.
2. K. Meguro, T. Kondo, O. Yodar, *J. Chem. Soc. Jpn., Pure Chem. Sec.*, 1956, 77, 1236.
3. E. D. Goddard and G. C. Benson, *Can. J. Chem.*, 1957, **35**, 986.
4. B. D. Flockhart, *J. Colloid Sci.*, 1957, **12**, 557.
5. K. J. Mysels and L. H. Princen, *J. Phys. Chem.*, 1959, **63**, 1696.
6. S. Miyamato, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 371.
7. K. J. Mysels and R. J. Otter, *J. Colloid Sci.*, 1961, **16**, 462.
8. J. M. Corkill and J. F. Goodman, *Trans. Faraday Soc.*, 1962, **58**, 206.
9. I. Satake, I. Iwamatsu and S. Hosokawa and R. Matuura, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 204.
10. K. Shirahama and R. Matuura, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 373.
11. M. Hato and K. Shinoda, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3889.
12. Y. Moroi, K. Motomura and R. Matuura, *J. Colloid Interface Sci.*, 1974, **46**, 111.
13. R. P. Varma, H. K. Bhargava and R. Dayal, *Pol. J. Chem.*, 1976, **50**, 307.
14. R. P. Varma and R. Dayal, *J. Chem. Phys. Phys. Chem. Biol.*, 1977, **74**, 443.
15. R. P. Varma and K. Kumar, *J. Am. Oil Chem. Soc.*, 1977, **54**, 156.
16. R. P. Varma and K. Kumar, *Colloid Polym. Sci.*, 1978, **256**, 266.
17. R. P. Varma and H. K. Bhargava, *J. Indian Chem. Soc.*, 1979, **56**, 680.
18. K. Shinoda, *J. Phys. Chem.*, 1954, **58**, 1136.
19. H. N. Singh, *et al.*, *J. Colloid Interface Sci.*, 1977, **59**, 386.
20. R. P. Varma and P. Bahadur, *J. Am. Oil Chem. Soc.*, 1974, **51**, 545.
21. R. P. Varma and P. Bahadur, *Indian J. Chem.*, 1972, **10**, 1180.
22. R. P. Varma and P. Bahadur, *Cellul. Chem. Technol*, 1975, **9**, 393.
23. R. P. Varma and P. K. Jain, *Pol. J. Chem.*, 1980, **54**, 561.
24. R. P. Varma and (Km.) Abha, *Bull. Soc. Chim. Fr.*, in the press.
25. B. W. Barry and G. F. J. Russel, *J. Colloid Interface Sci.*, 1974, **40**, 174.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 770-773

Studies on Polarographic Maxima of Nitrobenzaldehydes and Their Suppression by Some Ionic and Non-Ionic Surfactants

KAILASH CHANDRA, (Miss) INDU BALA and MUKHIAR SINGH

Department of Chemistry, Agra College Agra-282 002

Manuscript received 1 September 1982, accepted 15 August 1984

Role of some ionic and non-ionic surfactants in the suppression of polarographic negative maxima of *m*- and *p*-nitrobenzaldehydes (*ortho*-isomer does not yield maximum), in 4% (v/v) ethanolic solution has been studied at 25±0.1° in BR buffer of *p*H 7.0. It is observed that all types of surfactants (cationic, anionic and non-ionic) suppress the maxima, the cationic ones being the most effective. Their characteristic properties, *viz.* maximum suppression point (M.S.P.), specific suppression coefficient (S.S.C.) and critical micelle concentration (C.M.C.) have been determined. Relative efficacies of cationic, anionic and non-ionic surfactants in the suppression of the negative maxima of *m*- and *p*-nitrobenzaldehydes have been determined on the basis of M.S.P. values.

HOLLECK and Exner[1] studied the effect of tylose, a surfactant, on the polarographic reduction waves of *m*- and *p*-nitrobenzaldehydes at different *p*H and observed that it not only suppressed the maxima but also altered the mechanism of the electrode process. However, studies on the polarographic maxima of nitrobenzaldehydes and their suppresssion by ionic surfactants and also by widely used non-ionic surfactants, such as Triton X-100 and gelatin have not been undertaken so far, and the title investigation has therefore been undertaken.

Experimental

The depolarizers, *m*- and *p*-nitrobenzaldehydes (AnalaR) were recrystallized from ethanol before use. The other chemicals used were of AnalaR grade. The concentration of each of the depolarizers in the solution was kept at $1.0\times10^{-3}M$ (in 4% ethanol). BR buffer of *p*H 7.0 acted as a supporting electrolyte.

A Toshniwal CLO2 manual polarograph in conjunction with a Toshniwal PL 50 polyflex galvanometer was used. All the measurements were made at 25±0.1°. Purified nitrogen was used for deaeration. The potentials were measured against S.C.E. The d.m.e. had the following characteristics (in 0.1 *M* KCl, open circuit), $h_{corr}=62.4$ cm ; $m=3.0$ mg sec^{-1} ; $t=3.02$ sec ; $m^{2/3}t^{1/6}=2.504$ mg$^{2/3}$sec$^{-1/2}$. The number of electrons (*n*) involved in the reduction process was determined by millicoulometric method of DeVries and Kroon[2], which gave the value of *n* equal to 6 for *m*-nitrobenzaldehyde and 8 for *p*-nitrobenzaldehyde at *p*H 7.0.

The surfactants used were laurylpyridinium chloride (LPC), cetylpyridinium chloride (CPC), cetylpyridinium bromide (CPB), cetyldimethylbenzylammonium chloride (CDBAC) and cetyltrimethylammonium bromide (CTAB) (all cationic) ; dodecylbenzene sulphonate (DBS), sodium lauryl sulphate (SLS), Tergitol-7, Manoxol-OT and Manoxol-IB (all anionic) ; and Triton X-100, gelatin, Decon-90, ethyldigol and 2-ethoxyethanol (all non-ionic).

Results and Discussion

Representative Fig. 1 depicts the morphology of C – V curves of *m*-nitrobenzaldehyde in the presence of increasing concentrations of LPC.

m-/*p*-Nitrobenzaldehydes under the chosen experimental conditions yield sharp maxima which lie at –0.65 and –0.53 V (*vs* S.C.E.), respectively from the potential of the electrocapillary zero, which is –0.34 V (S.C.E.) under the same experimental conditions. However, *ortho*-isomer does not yield a maximum under these experimental conditions. The maxima of *m*- and *p*-nitrobenzaldehydes lie on the negative side of the electrocapillary zero and hence these are of negative polarity[3]. The relative heights of the maxima are in the following order, *m*-nitrobenzaldehyde>*p*-nitrobenzaldehyde.

Effect of increasing concentrations of surfactants on the maxima : The effect of increasing concentrations of cationic, anionic and non-ionic surfactants on E_{max} and i_{max} has been studied and the values are listed in Table 1. A perusal of this Table reveals that E_{max} of both of the maxima gets shifted to less negative potentials (positive shift) as the concentration of cationic, anionic and non-ionic surfactants is increased. The decrease in the value of i_{max} from the stage when no surfactant is present to the point preceding the elimination of the maxima

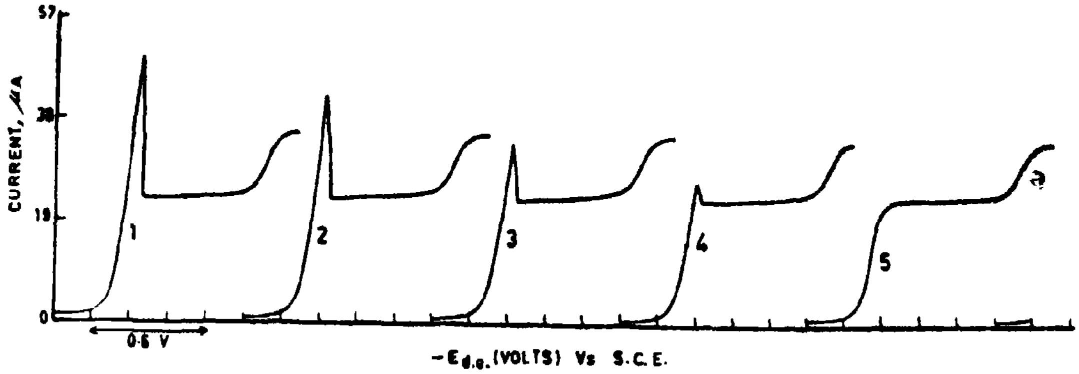


Fig. 1. C—V Curves of *m*-nitrobenzaldehyde in the presence of increasing concentrations of LPC. Each curve starts at −0.2 V.

TABLE 1—EFFECT OF IONIC AND NON-IONIC SURFACTANTS ON THE MAXIMA OF *m*- AND *p*-NITROBENZALDEHYDES IN BR BUFFER OF *p*H 7.0

m-Nitrobenzaldehyde [Surfactant] *M*	$-E_{max}$ V (S.C.E.)	i_{max} μA	*p*-Nitrobenzaldehyde [Surfactant] *M*	$-E_{max}$ V (S.C.E.)	i_{max} μA
0	0.65	49.40	0	0.53	29.40
$\times 10^5$		LPC	$\times 10^6$		
0.5	0.64	42.56	1.0	0.52	25.20
1.0	0.63	33.44	3.0	0.51	22.40
1.5	0.62	26.60	6.0	0.50	19.25
2.0 I step	0.538*	21.28+	8.0 I step	0.460*	17.85+
II step	1.330*	9.88+	II step	1.282*	10.50+
			III step	1.615*	7.00+
$\times 10^5$		CPC	$\times 10^6$		
0.5	0.65	40.66	1.0	0.53	25.90
1.0	0.64	32.68	3.0	0.52	23.10
1.5	0.64	28.50	6.0	0.50	18.90
2.0 I step	0.535*	21.28+	7.0 I step	0.463*	17.05+
II step	1.350*	9.88+	II step	1.286*	10.50+
			III step	1.612*	7.00+
$\times 10^4$		CPB	$\times 10^6$		
0.2	0.64	43.70	2.0	0.53	26.25
0.5	0.62	34.20	4.0	0.52	22.05
1.0	0.60	25.08	6.0	0.51	18.90
2.0 I step	0.530*	19.76+	7.0 I step	0.462*	17.85+
II step	1.338*	9.88+	II step	1.282*	10.50+
			III step	1.515*	7.00+
$\times 10^5$		CDBAC	$\times 10^6$		
0.5	0.64	37.24	1.0	0.52	27.30
0.7	0.64	31.92	2.0	0.52	22.75
0.9	0.63	26.60	4.0	0.50	19.25
1.0 I step	0.540*	20.52+	5.0 I step	0.470*	17.50+
II step	1.340*	9.88+	II step	1.290*	10.15+
			III step	1.620*	6.65+
$\times 10^6$		CTAB	$\times 10^6$		
0.2	0.65	40.66	0.5	0.52	26.95
0.5	0.64	30.40	0.8	0.51	23.45
0.7	0.62	26.22	1.0	0.50	19.60
1.0 I step	0.547*	20.52	2.0 I step	0.460*	17.85+
II step	1.320*	10.64	II step	1.288*	10.50+
			III step	1.614*	7.00+
$\times 10^5$		DBS	$\times 10^5$		
1.0	0.64	40.28	2.0	0.53	28.00
3.0	0.62	33.44	5.0	0.52	21.70
4.0	0.62	27.36	7.0	0.52	18.55
8.0 I step	0.545*	19.76+	8.0 I step	0.490*	17.50+
II step	1.320*	10.64+	II step	1.320*	10.15+
			III step	1.630*	6.65+

(*Table 1 contd.*)

m-Nitrobenzaldehyde [Surfactant] *M*	$-E_{max}$ V (S.C.E.)	i_{max} μA	*p*-Nitrobenzaldehyde [Surfactant] *M*	$-E_{max}$ V (S.C.E.)	i_{max} μA
$\times 10^4$		SLS	$\times 10^4$		
2.0	0.64	39.90	0.5	0.52	27.65
4.0	0.63	31.16	0.9	0.52	23.80
6.0	0.62	25.84	1.8	0.51	19.25
8.0 I step	0.540*	20.54+	3.0 I step	0.470*	17.50+
II step	1.352*	9.88+	II step	1.305*	9.80+
			III step	1.620*	6.65+
$\times 10^4$		Tergitol-7	$\times 10^4$		
0.2	0.64	43.32	1.0	0.53	26.60
0.5	0.63	36.48	3.0	0.52	23.10
0.8	0.62	27.36	7.0	0.51	18.90
1.0 I step	0.547*	20.14+	8.0 I step	0.480*	17.15+
II step	1.345*	9.12+	II step	1.315*	9.80+
			III step	1.610*	5.60+
$\times 10^4$		Manoxol-OT	$\times 10^4$		
0.4	0.64	43.32	2.0	0.52	26.95
0.6	0.63	33.06	5.0	0.51	22.05
0.8	0.62	28.12	8.0	0.50	19.25
1.0 I step	0.500*	19.76+	9.0 I step	0.465*	17.85+
II step	1.320*	10.64+	II step	1.285*	10.50+
			III step	1.518*	7.00+
$\times 10^3$		Manoxol-IB	$\times 10^3$		
0.3	0.65	42.56	2.0	0.51	26.25
0.5	0.64	38.00	4.0	0.51	21.35
2.0	0.60	28.12	6.0	0.50	19.60
4.0 I step	0.530*	20.14+	7.0 I step	0.468*	17.50+
II step	1.320*	10.64+	II step	1.300*	9.80+
			III step	1.580*	6.85+
$\times 10^4$		Triton X-100**	$\times 10^4$		
2.0	0.64	42.94	0.8	0.53	26.60
4.0	0.62	32.68	2.0	0.52	23.45
6.0	0.61	26.50	5.6	0.52	18.90
7.0 I step	0.530*	20.90+	7.0 I step	0.485*	17.15+
II step	1.335*	9.88+	II step	1.310*	9.45+
			III step	1.620*	6.65+
$\times 10^3$		Gelatin**	$\times 10^3$		
0.5	0.64	38.00	0.4	0.52	27.30
0.9	0.64	30.40	0.6	0.52	22.05
2.5	0.62	25.00	0.9	0.51	18.55
3.0 I step	0.530*	20.52+	1.0 I step	0.485*	16.80+
			II step	1.290*	9.80+
			III step	1.632*	6.30+
$\times 10^3$		Decon-90**	$\times 10^3$		
1.0	0.64	43.32	0.3	0.52	25.90
2.0	0.62	34.20	0.6	0.52	22.40
5.0	0.60	26.60	0.9	0.51	18.90
7.0 I step	0.538*	20.52+	1.0 I step	0.486*	17.15+
II step	1.320*	9.96+	II step	1.385*	9.45+
			III step	1.635*	5.95+

(Table 1 contd.)

× 10[3]		Ethyldigol		× 1.**			
0.2		0.64	40.28	0.7		0.52	26.25
0.4		0.62	32.68	1.0		0.50	22.75
0.6		0.60	26.60	2.0		0.51	19.25
1.0	I step	0.540*	20.52+	3.0	I step	0.476*	17.15+
	II step	1.320*	10.64+		II step	1.312*	9.45+
					III step	1.632*	6.65+
× 10[1]		2-Ethoxyethanol		× 10[1]			
0.6		0.60	44.08	1.0		0.50	26.60
1.5		0.56	37.24	3.0		0.49	23.10
2.5		0.54	25.84	4.2		0.49	18.20
8.0	I step	0.530*	16.72+	5.0	I step	0.460*	17.15+
	II step	1.320*	10.26+		II step	1.288*	9.80+
					III step	1.560*	5.60+

* value of $E_{1/2}$, + value of i_d, and
** concentrations expressed in percentage.

is different for both the isomers. The decrease in i_{max} is in the following order, *m*-nitrobenzaldehyde> *p*-nitrobenzaldehyde.

After the suppression of the maxima by requisite amounts of the surfactants, each depolarizer yields a well-defined wave [Fig. 1 (6)] which is diffusion-controlled and irreversible.

Characteristic properties of the surfactants vis-a-vis *their relative efficacies in suppression of the maxima of* m- and p-*nitrobenzaldehydes :* The values of characteristic properties, *viz.* M.S.P., S.S.C. and C.M.C. of the surfactants in respect to the maxima of *m*- and *p*-nitrobenzaldehydes were determined[4-6] and have been listed in Table 2. A perusal of this Table reveals that M.S.P. and S.S.C. values for cationic surfactants are much less than those for anionic ones. It follows from this that the amount of ionic surfactants required to suppress maxima of similar sign is greater than those possessing dissimilar charges[7].

Antweiler[8] has unambiguously proved that the polarographic maxima of the first kind are due to tangential streaming of the solution with respect to the drop. The success of a maxima suppressor depends on its capability of curbing this streaming. Since the maxima in the present study lie on the negative side of the electro-capillary zero, the cationic surfactants will move right up to the mercury surface and the anionic ones are likely to move at a distance somewhere in the double layer. A cationic surfactant will prevent streaming more effectively as compared to an anionic one with identical hydrocarbon chain. This is supported by the fact that LPC is more effective than SLS, though both the surfactants have the same carbon chain length.

On the basis of M.S.P. values, the order of relative efficacies of cationic, anionic and non-ionic surfactants in suppressing the negative maxima of *m*- and *p*-nitrobenzaldehydes has been established as follows :

Cationic surfactants : LPC and CPC possess the same polar head but different carbon chain length. The following order exists for their efficacies : CPC > LPC. Thus, with the same polar head the efficacy of a cationic surfactant increases with the increase in carbon chain length.

In the case of CTAB and CDBAC which possess the same carbon chain length but different polar head, it is found that the former is more effective than the latter. The efficacies of cationic surfactants are in the following order, CTAB > CDBAC > CPC > LPC > CPB.

Anionic surfactants : In the case of Manoxol-IB and Manoxol-OT which possess the same polar head but different carbon chain lengths, it is found that the latter with longer carbon chain is more effective in suppressing these negative maxima. The efficacies of the anionic surfactants are in the following order, SLS>DBS>Tergitol-7>Manoxol-OT>Manoxol-IB.

Non-ionic surfactants : Non-ionic or amphoteric substances suppress maxima on the basis of preferential adsorption on the mercury drop. The

TABLE 2—M.S.P., S.S.C. AND C.M.C. VALUES FOR IONIC AND NON-IONIC SURFACTANTS IN RESPECT OF THE MAXIMA OF *m*- AND *p*-NITROBENZALDEHYDES

Surfactants	*m*-Nitrobenzaldehyde			*p*-Nitrobenzaldehyde		
	M.S.P. *M*	S.S.C. *M*	C.M.C. *M*	M.S.P. *M*	S.S.C. *M*	C.M.C. *M*
LPC	1.8×10^{-5}	5.3×10^{-6}	8.0×10^{-6}	7.0×10^{-9}	2.4×10^{-9}	3.0×10^{-9}
CPC	1.7×10^{-5}	5.1×10^{-6}	7.0×10^{-6}	6.8×10^{-9}	2.0×10^{-9}	4.0×10^{-9}
CPB	2.0×10^{-5}	5.4×10^{-6}	4.0×10^{-6}	7.0×10^{-9}	3.1×10^{-9}	5.0×10^{-9}
CDBAC	9.2×10^{-5}	4.0×10^{-6}	5.0×10^{-6}	4.8×10^{-9}	1.6×10^{-9}	2.0×10^{-9}
CTAB	9.0×10^{-6}	3.5×10^{-6}	5.0×10^{-6}	2.0×10^{-9}	7.0×10^{-9}	8.0×10^{-9}
DBS	7.9×10^{-5}	2.3×10^{-5}	4.3×10^{-5}	7.5×10^{-5}	2.5×10^{-6}	4.3×10^{-5}
SLS	7.1×10^{-5}	1.2×10^{-5}	3.5×10^{-5}	2.8×10^{-5}	8.0×10^{-6}	9.0×10^{-6}
Tergitol-7	9.7×10^{-5}	5.3×10^{-5}	4.0×10^{-5}	7.8×10^{-5}	2.8×10^{-5}	2.3×10^{-5}
Manoxol-OT	1.0×10^{-4}	5.7×10^{-5}	5.2×10^{-5}	8.9×10^{-5}	3.5×10^{-5}	5.4×10^{-5}
Manoxol-IB	3.9×10^{-3}	9.2×10^{-3}	1.5×10^{-3}	6.4×10^{-5}	2.5×10^{-3}	4.0×10^{-3}
Triton X-100*	6.9×10^{-4}	8.5×10^{-4}	—	6.6×10^{-4}	9.5×10^{-5}	—
Gelatin*	2.9×10^{-3}	7.4×10^{-4}	—	9.9×10^{-4}	5.3×10^{-4}	—
Decon-90*	5.5×10^{-3}	1.9×10^{-2}	—	9.8×10^{-3}	3.2×10^{-3}	—
Ethyldigol	1.0×10^{-2}	3.8×10^{-2}	—	2.8×10^{-2}	8.9×10^{-2}	—
2-Ethoxyethanol	7.8×10^{-1}	2.0×10^{-1}	—	4.9×10^{-1}	1.8×10^{-1}	—

* M.S.P., S.S.C. and C.M.C. values in percentage.

/ of these suppressors depends upon the ial range of the maxima. Different non-suppressors are adsorbed on the mercury :o different extent at a given potential. The of the efficacies is as follows, Triton X-100> >Decon-90>ethyldigol> 2-ethoxyethanol.

vledgement

ɪnks are due to the Principal, Agra College ilities and to U.G.C., New Delhi for a Senior :h Fellowship to one of the authors (K.C.).

References

1. L. Holleck and H. J. Exner, *Chem. Abst.*, 1952, **46**, 6913.
2. T. DeVries and J. L. Kroon, *J. Am. Chem. Soc.*, 1953, **75**, 2484.
3. J. Heyrovsky and J. Kuta, "Principles of Polarography", Academic Press, New York, 1966, p. 437.
4. E. L. Colichman, *J. Am. Chem. Soc.*, 1950, **72**, 4036.
5. G. Semerano, *Arch. Sci. Biol.* (*Italy*), 1934, **20**, 825.
6. G. Ram and M. Singh, *J. Indian Chem. Soc.*, 1975, **52**, 469.
7. W. U. Malik and R. Haque, *J. Polarogr. Soc.*, 1962, **8**, 86.
8. H. J. Antweiler, *Z. Electrochem.*, 1937, **43**, 596 ; 1938, **44**, 719, 831, 888

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 774-776

Effect of Temperature on Intrinsic Viscosity of Partially Hydrolysed Polyacrylamide

NIMAI CHANDRA DEY

Saldiha College, Saldiha, Bankura

Manuscript received 27 February 1984, accepted 21 July 1984

Two partially hydrolysed polyacrylamides, Pusher 500 and Pusher 700 have been studied. These high molecular weight water-soluble polymers show pronounced change in rheological properties under the varying conditions of electrolyte concentrations. Intrinsic viscosity of the polymers decreases with increase of electrolyte concentrations and shows the linear relationship with reciprocal of temperature.

However, higher molecular weight and lower degree of hydrolysed polyacrylamide, Pusher 700 shows more dramatic effect than Pusher 500, which is attributed to the change in molecular size of the polymers in solution.

PARTIALLY hydrolysed polyacrylamides are recently extensively used as additives in water-flood for enhanced recovery of crude[1]. In other fields also, these water-soluble and high molecular weight polymers are receiving wide applications. Most of these applications are related to the rheology and molecular size of the polymers.

In order to understand the property, the effects of temperature changes on the intrinsic viscosity of dilute solutions of the partially hydrolysed polyacrylamides have been sutdied. Mandelkern and Flory[2] have considered the temperature dependence of intrinsic viscosities of cellulose tributyrate and tricaprylate, and Flory *et al*[3] that of intrinsic viscosities of cellulose acetates and cellulose trinitrate in terms of current hydrodynamic and thermodynamic theories of polymer solutions which relate viscosity and chain configuration. The large negative temperature coefficients observed were ascribed to increases in chain flexibility. Other approaches to the problem have also been made. Manley[4] interpreted changes in intrinsic viscosities of ethyl hydroethyl cellulose fractions with temperature in terms of varying degree of hydration. Howlett *et al.*[5] reported a linear relationship between the logarithm of the relative viscosity and reciprocal of absolute temperature for dilute solutions of secondary cellulose acetate. In this paper, the temperature dependence of intrinsic viscosities has been discussed briefly in terms of current hydrodynamic and thermodynamic theories.

Experimental

Pusher 500 and Pusher 700 (Dow Chemical, U.S.A.), the high molecular weight water-soluble partially hydrolysed polyacrylamides, were used in the study. Their molecular characteristics were determined by viscosity method[6] and are given in Table 1.

TABLE 1—MOLECULAR CHARACTERISTICS OF PUSHER 500 AND PUSHER 700

Polymer	Molecular weight** $\times 10^6$	Degree of hydrolysis† %	Calculated extended polymer chain length*, μ
Pusher 500	3-4 (n = 490)	37 (a = 63, c = 37)	12.25
Pusher 700	4.5-5.5 (n = 701)	31 (a = 69, c = 31)	17.5

* Length of one mer unit $CH_2-CH\ CONH_2$ or $CH_2-CH.COOH$ taken as 2.5 Å.

** n = 100 times repeating unit of monomer.

† a = Amide monomer unit %, c = carboxyl monomer unit %.

Solutions of dry polymer were prepared by adding them slowly to NaCl solutions. The solution was stirred with magnetic stirrer at a low speed and kept overnight to ensure complete hydration. A 0.5 ml formaldehyde (37%) was added to 1 dm^3 of the solution to prevent bacterial and oxidative degradation, if any. Viscosities of the solvent and polymer solution in the concentration range of 100 to 900 ppm were measured at several temperatures in the range of 30 to 60°. Capillary viscometers used were of such dimensions as to eliminate shear effects[7]. Measurements were made in thermostatically controlled water-bath maintained to ±0.02°. All solutions were filtered before use.

Results and Discussion

Partially hydrolysed polyacrylamides are long chain high molecular weight linear polymers and made up of acrylamide and acrylic acid monomer units. The structure of the polymer reveals that due to presence of negative groups, *viz.* carboxylate, the polymer chain is extended by electrostatic repulsion and the polymer as a whole changes from nearly spherical to elongated form[8].

Intrinsic viscosities of dilute solutions of Pusher 500 and Pusher 700 at different temperatures and salinities are given in Table 2 obtained from the extrapolation of the plot of reduced viscosity *vs* polymer concentration. The intrinsic viscosities are also plotted against 1/T for Pusher 500 and Pusher 700 at three saline concentrations and the plots are given in Fig. 1.

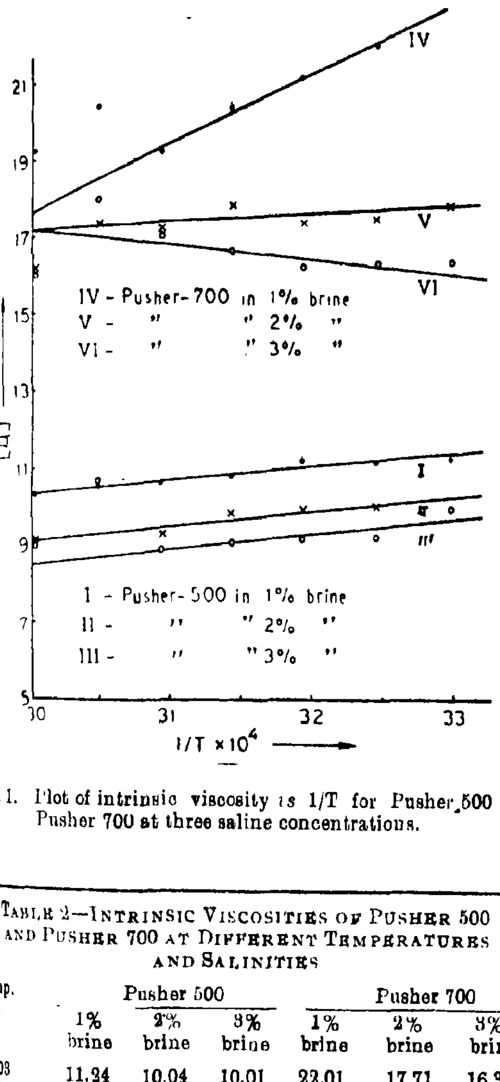


Fig. 1. Plot of intrinsic viscosity *vs* 1/T for Pusher 500 and Pusher 700 at three saline concentrations.

TABLE 2—INTRINSIC VISCOSITIES OF PUSHER 500 AND PUSHER 700 AT DIFFERENT TEMPERATURES AND SALINITIES

Temp. K	Pusher 500			Pusher 700		
	1% brine	2% brine	3% brine	1% brine	2% brine	3% brine
303	11.24	10.04	10.01	22.01	17.71	16.34
308	11.14	10.00	9.21	21.95	17.47	16.27
313	11.15	9.89	9.15	21.09	17.34	16.23
318	10.85	9.78	9.10	20.32	17.82	16.60
323	10.60	9.80	8.92	19.21	17.20	16.96
328	10.59	10.58	10.67	20.38	17.30	17.99
333	10.31	9.12	9.01	19.24	16.22	16.08

The temperature dependence of intrinsic viscosity, $[\mu]$ follows the equation[7]

$$[\mu] = \text{Ke}\, M/RT - \text{Ka}M^{\alpha} \tag{1}$$

where, M = molecular weight of the polymer ; R = universal gas constant ; Ke, Ka and α = constants ; T = absolute temperature. Our experimental data obeys the above equation as shown in Fig. 1. This indicates that $[\mu]$ is a linear function of 1/T for high molecular weight polymers also.

Intrinsic viscosity of the polymer is related to the molecular size of the polymer[8]

$$\sqrt{\overline{r^2}} = 8(M[\mu])^{1/3} \tag{2}$$

$\sqrt{\overline{r^2}}$, the root mean square end-to-end distance of the polymer chain (often called polymer molecular diameter) is a function of intrinsic viscosity of the polymer solutions. Plots of $[\mu]$ *vs* 1/T shows that intrinsic viscosity decreases with temperature except for Pusher 700 in 3% brine solution. This dependence is directly connected with the temperature coefficient of the thermodynamic affinity of the solvent for the polymer. If thermodynamic affinity improves as temperature rises, the coil swells more and $[\mu]$ increases with an elevation of temperature, the opposite effect is played if the affinity diminishes with the temperature rise[9,10].

The polymers under study contains both amide and carboxyl groups in their chain which are highly polar in character. The water molecules in the solvent are attached to the polymer by dipole-dipole attraction and the hydrogen bonding through nitrogen-oxygen and oxygen-oxygen atoms[8]. As the temperature rises, the attachment of the solvent molecules decreases and the polymer molecules suffer a decrease in solvent affinity, and so the intrinsic viscosity decreases with temperature. The electrostatic repulsion which is the cause of polymer chain extension is screened at least partially by the presence of electrolyte. As a result of which the extension of the chain is effected.

For both the polymers at all the temperatures, the intrinsic viscosity is found dramatically lower with the increase of electrolyte concentration in the polymer solution. It is evident (Fig. 1) that molecular size (which is proportional to $[\mu]$) surprisingly decreases with the higher electrolyte content. The saline effect is more predominant in Pusher 700 than in Pusher 500. The effect is so pronounced that at 3% brine concentration, the polymer chain is so contracted that $[\mu]$ increases with temperature. At this condition, the thermodynamic affinity actually improves with the rise of temperature.

Acknowledgement

The author is thankful to Dow Chemical Company, U.S.A. for their keen interest in the research programme, and to U.G.C., New Delhi for the sanction of the project.

References

1. N. C. DEY, Ph.D. Thesis, Indian School of Mines, Dhanbad, 1980.
2. L. MANDELKERN and P. J. FLORY, *J. Am. Chem. Soc.*, 1952, **74**, 2517.
3. P. J. FLORY, O. K. SPURR and D. K. CARPENTER, *J. Polym. Sci.*, 1958, **27**, 231.
4. B. ST. J. MANLEY, *Arkiv Kemi*, 1956, **9**, 519.

5. F. HOWLETT, E. MINSHALL and A. R. URQUHART, *J. Text. Inst.*, 1944, **35**, T133.
6. P. J. FLORY, "Principles of Polymer Chemistry", Carnel Univ. Press, Ithaca, 1953, Chap. 14.
7. W. R. MOORE in "Progress in Polymer Science", ed. A. D. JENKIN, Pergamon Press, Oxford, 1967, Vol. I, p. 27.
8. N. C. DEY and A. K. SRIVASTAVA, *Hung. J. Ind. Chem.*, 1980, **8**, 3/5.
9. J. NIEZETTE, N. HADJICHRISTIDIS and V. DESREUX, *Eur. Polym. J.*, 1977, **13**, 41.
10. F. W. BILLMEYER, JR., "Text Book of Polymer Chemistry", John Wiley, New York, 1971, p. 84.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 777-780

Anion Exchange Separation of Some Metal Ions in Aqueous-Acetone-Trichloroacetic Acid Media. Part—IV

S. V. KULKARNI*, S. S. JOSHI and S. K. SOMAN

Department of Chemistry, Shivaji University, Kolhapur-416 004

Manuscript received 29 September 1983, revised 30 May 1984, accepted 10 August 1984

Anion exchange chromatographic studies of Cd^{II}, Zn^{II}, Co^{II}, Cu^{II}, Ca^{II}, Mn^{II}, Mg^{II} and Ni^{II} on Dowex 21 K (Cl^- form) in mixed solvent systems were carried out. The efficiency of acetone-trichloroacetic acid (TCA) system is evaluated in terms of distribution coefficients and suggested the following selectivity sequence,

$$Cd \gg Zn > Co > Cu > Ca > Mn \approx Mg \approx Ni.$$

Methods have been developed for the separation of Ca/Mn/Mg/Ni from Cd/Zn/Co in binary mixtures. Many interesting sequential separations of metal ions from tertiary and quaternary mixtures are carried out. This ion exchange method is applied to the analysis of brass.

ION-exchange characteristics of metal ions have been studied in carboxylic acid media and several metal ions have successfully been separated on anion exchange resins. Anion exchange studies in buffered aqueous solutions of acetic, chloroacetic and dichloroacetic acid containing acetone were reported earlier[1-3]. A systematic anion exchange chromatographic study of Co^{II}, Ni^{II}, Zn^{II}, Mn^{II}, Mg^{II}, Ca^{II}, Cu^{II} and Cd^{II} on Dowex 21 K in mixed water-acetone-trichloroacetic acid (TCA) solvent system is presented in this paper. The results include the separation of metal ions from binary, tertiary and quaternary mixtures and the technique is applied to the analysis of brass alloy.

Experimental

An anion exchange resin, Dowex 21 K in chloride form was used for all anion exchange distribution studies. The solutions of Co^{II}, Ni^{II}, Zn^{II}, Mn^{II}, Mg^{II}, Ca^{II}, Cu^{II} and Cd^{II} were prepared by dissolving their chlorides in distilled water and standardized complexometrically[4].

Distribution studies were carried out using solutions (50 ml each) containing the metal ion and a mixture consisting of acetone, TCA and water. To this mixture 1 g resin was added and the batches were equilibrated by shaking for 24 h. The resin was filtered off and the filtrate was analysed for the metal ions. The distribution coefficients, K_D were calculated by using the equation

$$K_D = \frac{\text{meq.metal per g dry resin}}{\text{meq.metal per ml solution}}$$

For the chromatographic separations, the resin bed was prepared by making a slurry of the resin ($\approx$15 g) in water and transferred to the graduated column. The synthetic mixture of metal ions was fed on the column. The metal ions were eluted by suitable eluting agents (Tables 3-5). From the binary mixtures Mg/Cu/Mn/Ca/Ni-Co, Mg/Cu/Mn/Ca/Ni were eluted by 80% acetone-3 *M* TCA (eluent e) and Co was eluted by distilled water (eluent f). The mixtures Cu/Co/Mn/Ni/Mg/Ca-Cd were analysed and Cu/Co were eluted by 80% acetone +0.5 *M* TCA (eluent a), Mn/Ni/Mg/Ca by 60% acetone +0.5 *M* TCA (eluent d), and Cd by 50% acetone +0.1 *M* TCA (eluent c). Cu/Co/Mg/Ca were eluted by eluent a, Mn/Ni by eluent d, and Zn by 20% acetone +0.5 *M* TCA (eluent b) from the binary mixture Cu/Co/Mg/Ca/Mn/Ni-Zn. From tertiary mixtures Mg/Cu/Mn/Ca/Ni were eluted by eluent e, Co by 60% acetone +3 *M* TCA (eluent h), and Zn/Cd by eluent d and c, respectively. From quaternary mixtures Mg/Ca/Mn/Cu and Ni were eluted by eluent e, Co by eluent h, Zn by 0.1 *M* HCl (eluent g), and Cd by eluent c, and the effluents were estimated in 10 ml fractions.

Results and Discussion

The distribution coefficients of the metal ions under study were found out at 0.5, 1, 2, 3 *M* of TCA and 0, 20, 40, 60, 80 percentages of acetone. As most of the binary, tertiary, quaternary mixture separations are possible in 0.5 and 3 *M* TCA, the distribution coefficients only in these media are reported in Tables 1 and 2.

The effect of the concentration of TCA to the metal ion uptake by an anion exchanger is seen from the results presented in Tables 1 and 2. K_D values of Ni^{II}, Mn^{II}, Mg^{II} are low at 0.5 and 1 *M* TCA at all percentages of acetone, indicating the tendency of these ions to form less stable anionic complexes or not to form such complexes. This behaviour may lead to lesser or no exchange on an anion exchanger. The distribution coefficients of Zn^{II}, Cd^{II}, Co^{II} and Cu^{II} at 3 *M* TCA are greater than

TABLE 1—ANION EXCHANGE DISTRIBUTION COEFFICIENTS IN AQUEOUS ACETONE-TRICHLOROACETIC ACID (0.5 *M*) ON DOWEX 21 K (Cl^{-1})

Ion	Acetone concentration % (v/v)				
	0	20	40	60	80
Co^{II}	15	18	14	18	17
Ni^{II}	NA	NA	NA	NA	NA
Zn^{II}	18	25	31	59	788
Mn^{II}	3	1	3	NA	NA
Mg^{II}	NA	3	NA	2	NA
Ca^{II}	28	29	29	32	28
Cu^{II}	19	25	32	19	25
Cd^{II}	NA	NA	3	97	513

TABLE 2—ANION EXCHANGE DISTRIBUTION COEFFICIENTS IN AQUEOUS ACETONE-TRICHLOROACETIC ACID (3 *M*) ON DOWEX 21 K (Cl^{-1})

Ion	Acetone concentration % (v/v)				
	0	20	40	60	80
Co^{II}	82	91	108	134.6	2460
Ni^{II}	NA	3	3	3	5
Zn^{II}	52	86	102	206	5468
Mn^{II}	2	2	2	4	4
Mg^{II}	NA	NA	NA	NA	NA
Ca^{II}	12	16	16	24	27
Cu^{II}	62	62	82	103	140
Cd^{II}	32	102	186	690	5104

those at 0.5 *M* TCA at respective acetone percentages. Cu^{II} shows *considerable rise* (≅3 *to* 4 *times*) in K_D at 3 *M* TCA indicating increasing tendency of complex formation at higher concentration of the acid.

The distribution coefficients of Zn^{II}, Co^{II}, Cd^{II} increase with the rise in acetone concentration. The profound or better effect is observed in 40-80% acetone range and at 3 *M* TCA. This behaviour is according to the fact that the presence of a less polar solvent mixed with water enhances the extent of complex formation[5,6].

There is no measurable change in K_D values of Co^{II} in 0.5 *M* TCA, upto 60% acetone-1 *M* TCA. In 2 *M* TCA upto 40% acetone the value of K_D is ≃50, showing that the partition of metal ion in solvent and resin phase is nearly equal. The distribution coefficient increases continuously in 3 *M* TCA and reaches maximum (K_D = 2460) at 80% acetone. The same type of blue coloured anionic complex of Co^{II} was also obtained in 80% acetone-3 *M* acetic acid[1]/chloroacetic acid[2]/dichloroacetic acid[3]. Zn^{II} and Cd^{II} show maximum K_D under the same conditions. The K_D data of the metal ions in Tables 1 and 2 suggest the following selectivity sequence,

Cd > Zn > Ca > Cu > Co > Mn ≃ Mg ≃ Ni (0.5 *M* TCA)

Cd > Zn > Co > Cu > Ca > Mn ≃ Mg ≃ Ni (3 *M* TCA)

As compared to K_D data reported earlier[1-3] it is observed that Cu^{II} gives higher values in 3 *M* TCA than acetic, chloroacetic, dichloroacetic acids. The distribution tendencies of Cu^{II} on an anion exchanger is thus modified by TCA in presence of water miscible organic solvent (acetone).

The results of quantitative separation of synthetic binary, tertiary and quaternary mixtures are presented in Tables 3, 4 and 5, respectively. Mg, Cu, Mn, Ca and Ni are eluted first as these ions are weakly bound to the resin in comparison to Co, Cd

TABLE 3—QUANTITATIVE SEPARATION OF SYNTHETIC BINARY MIXTURES

FIRST ION IN THE MIXTURE IS ELUTED WHILE SECOND ION IS RETAINED

Sl. no.	Mixture	Metal ion eluted	Eluting agent*	m mol taken	m mol found
1.	$Mg^{II} + Co^{II}$	Mg^{II}	e	0.175	0.175
		Co^{II}	f	0.244	0.214
2.	$Cu^{II} + Co^{II}$	Cu^{II}	e	0.240	0.210
		Co^{II}	f	0.244	0.244
3.	$Mn^{II} + Co^{II}$	Mn^{II}	e	0.211	0.210
		Co^{II}	f	0.244	0.244
4.	$Ca^{II} + Co^{II}$	Ca^{II}	e	0.184	0.192
		Co^{II}	f	0.162	0.161
5.	$Ni^{II} + Co^{II}$	Ni^{II}	e	0.220	0.229
		Co^{II}	f	0.244	0.244
6.	$Cu^{II} + Cd^{II}$	Cu^{II}	a	0.256	0.252
		Cd^{II}	c	0.251	0.251
7.	$Mn^{II} + Cd^{II}$	Mn^{II}	d	0.230	0.226
		Cd^{II}	c	0.239	0.241
8.	$Co^{II} + Cd^{II}$	Co^{II}	a	0..50	0.249
		Cd^{II}	c	0.239	0.241
9.	$Ni^{II} + Cd^{II}$	Ni^{II}	d	0.262	0.260
		Cd^{II}	c	0.239	0.241
10.	$Mg^{II} + Cd^{II}$	Mg^{II}	d	0.250	0.211
		Cd^{II}	c	0.239	0.041
11.	$Ca^{II} + Cd^{II}$	Ca^{II}	d	0.241	0.240
		Cd^{II}	c	0.239	0.241
12.	$Cu^{II} + Zn^{II}$	Cu^{II}	a	0.256	0.252
		Zn^{II}	b	0.201	0.202
13.	$Co^{II} + Zn^{II}$	Co^{II}	a	0.234	0.246
		Zn^{II}	b	0.200	0.166
14.	$Mn^{II} + Zn^{II}$	Mn^{II}	d	0.230	0.228
		Zn^{II}	b	0.201	0.202
15.	$Ni^{II} + Zn^{II}$	Ni^{II}	d	0.262	0.261
		Zn^{II}	b	0.201	0.202
16.	$Mg^{II} + Zn^{II}$	Mg^{II}	a	0.248	0.252
		Zn^{II}	b	0.201	0.202
17.	$Ca^{II} + Zn^{II}$	Ca^{II}	a	0.254	0.268
		Zn^{II}	b	0.201	0.202

* Abbreviation as in Table 5.

TABLE 4—QUANTITATIVE SEPARATION OF SYNTHETIC TERNARY MIXTURES

Sl. no.	Mixture	Metal ion eluted	Eluting agent*	m mol taken	m mol found
1.	$Mg^{II} + Co^{II} + Zn^{II}$	Mg^{II}	e	0.204	0.154
		Co^{II}	h	0.162	0.161
		Zn^{II}	d	0.248	0.203
2.	$Cu^{II} + Co^{II} + Zn^{II}$	Cu^{II}	e	0.210	0.211
		Co^{II}	h	0.162	0.161
		Zn^{II}	d	0.243	0.203
3.	$Mn^{II} + Co^{II} + Zn^{II}$	Mn^{II}	e	0.210	0.200
		Co^{II}	h	0.162	0.161
		Zn^{II}	d	0.248	0.203
4.	$Ca^{II} + Co^{II} + Zn^{II}$	Ca^{II}	e	0.196	0.145
		Co^{II}	h	0.162	0.161
		Zn^{II}	d	0.243	0.208
5.	$Ni^{II} + Co^{II} + Zn^{II}$	Ni^{II}	e	0.245	0.259
		Co^{II}	h	0.162	0.161
		Zn^{II}	d	0.243	0.203
6.	$Mg^{II} + Co^{II} + Cd^{II}$	Mg^{II}	e	0.204	0.158
		Co^{II}	h	0.162	0.161
		Cd^{II}	c	0.242	0.223
7.	$Cu^{II} + Co^{II} + Cd^{II}$	Cu^{II}	e	0.210	0.221
		Co^{II}	h	0.162	0.161
		Cd^{II}	c	0.242	0.223
8.	$Mn^{II} + Co^{II} + Cd^{II}$	Mn^{II}	e	0.210	0.221
		Co^{II}	h	0.162	0.161
		Cd^{II}	c	0.242	0.223
9.	$Ca^{II} + Co^{II} + Cd^{II}$	Ca^{II}	e	0.196	0.148
		Co^{II}	h	0.162	0.161
		Cd^{II}	c	0.242	0.223
10.	$Ni^{II} + Co^{II} + Cd^{II}$	Ni^{II}	e	0.245	0.255
		Co^{II}	h	0.162	0.161
		Cd^{II}	c	0.242	0.228

* Abbreviation as in Table 5.

and Zn. The eluting agents for Mg, Cu, Mn, Ca and Ni depend on the other co-ion in binary mixtures (Table 3). The clear cut separation of Co/Ni/Mn/Mg/Ca/Cu-Cd is shown in Fig. 1. Co^{II} is eluted by distilled water, showing that decomplexation takes place quickly by the cheapest solvent like water. The element in tertiary mixtures are separated by selective sorption method. The first metal ion Mg/Cu/Mn/Ca/Ni is eluted by e, the second metal ion Co by h, and the third ion Zn/Cd is eluted by c and d, respectively. The separation of four metal ions is attempted and the successful results are obtained. In these ion-exchange separations the first metal is different, *i.e.* Mg or Ca or Mn or Cu or Ni, the other metal ions Co, Zn and Cd are common and are eluted by h, g, c, respectively. The separation of Mn/Cu/Ni is better than Mg/Ca from these tertiary mixtures.

TABLE 5—QUANTITATIVE SEPARATION OF SYNTHETIC QUATERNARY MIXTURES IN TCA

Sl. no.	Mixture	Metal ion eluted	Eluting agent*	m mol taken	m mol found
1.	$Mg^{II} + Co^{II} + Zn^{II} + Cd^{II}$	Mg^{II}	e	0.204	0.154
		Co^{II}	h	0.162	0.161
		Zn^{II}	g	0.203	0.164
		Cd^{II}	c	0.242	0.223
2.	$Ca^{II} + Co^{II} + Zn^{II} + Cd^{II}$	Ca^{II}	e	0.196	0.145
		Co^{II}	h	0.162	0.161
		Zn^{II}	g	0.203	0.164
		Cd^{II}	c	0.242	0.223
3.	$Mn^{II} + Co^{II} + Zn^{II} + Cd^{II}$	Mn^{II}	e	0.210	0.200
		Co^{II}	h	0.162	0.161
		Zn^{II}	g	0.203	0.164
		Cd^{II}	c	0.242	0.223
4.	$Cu^{II} + Co^{II} + Zn^{II} + Cd^{II}$	Cu^{II}	e	0.210	0.211
		Co^{II}	h	0.162	0.161
		Zn^{II}	g	0.208	0.164
		Cd^{II}	c	0.242	0.223
5.	$Ni^{II} + Co^{II} + Zn^{II} + Cd^{II}$	Ni^{II}	e	0.245	0.230
		Co^{II}	h	0.162	0.161
		Zn^{II}	g	0.203	0.164
		Cd^{II}	c	0.242	0.223

* a – 80% Acetone – 0.5 *M* TCA ; b – 20% acetone – 0.5 *M* TCA ; c – 50% acetone – 0.1 *M* TCA ; d – 60% acetone – 0.5 *M* TCA ; e – 80% acetone – 3 *M* TCA ; f – distilled water ; g – 0.1 *M* HCl , h – 60% acetone – 3 *M* TCA.

Analysis of standard brass sample : About 0.3 g brass alloy was weighed out accurately and dissolved by heating with HNO_3 and H_2SO_4 (1 : 1). Care was taken to remove all H_2SO_4 and the solution was finally fumed until only about 1 ml HNO_3 remained. After dilution, any remaining insoluble residue was separated by filteration, and the filtrate was kept for the column separation. The solution was passed through the column. The ion-exchange separation and the determinations of Cu and Zn were then carried out as described for the analysis of synthetic mixture. The separation of Cu and Zn from brass alloy was also carried out by standard procedure and Cu was estimated volumetrically[7] and zinc gravimetrically[7]. The results obtained by both the methods are presented in Table 6.

TABLE 6—ESTIMATION OF Cu^{II} AND Zn^{II} IN BRASS ALLOY

Method	Weight of alloy taken g	Amount of Cu g	% Cu	Amount of Zn g	% Zn
Standard method	0.358	0.217	61.3	0.133	37.6
Ion-exchange method	0.358	0.216	61.2	0.137	38.9

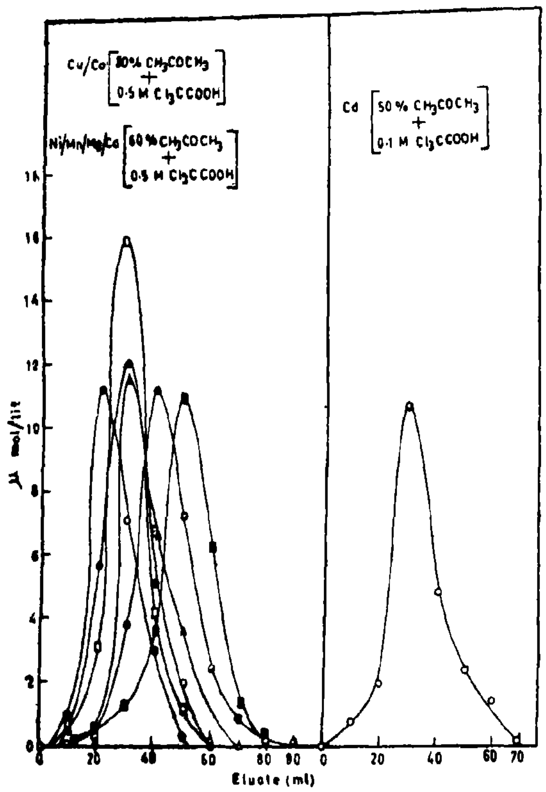


Fig. 1. Elution curves of Cu (—○—)/Co (—□—)/Ni (—⊖—)/ Mn (—●—)/Mg (—■—)/Ca (—Δ—)/Cd (—○—).

The described method provides an excellent means for the quantitative separation of Cu^{II} and Zn^{II} from each other and for the accurate determination of these elements in brass alloy. The attractive feature of the separation procedure is that only a single anion exchange column is employed and no further purification steps are necessary.

Acknowledgement

One of the authors (S.S.J.) is thankful to the C.S.I.R., New Delhi for the award of Senior Research Fellowship.

References

1. S. V. KULKARNI, S. K. SOMAN and S. S. JOSHI, *J. Indian Chem. Soc.*, 1983, **60**, 779.
2. S. V. KULKARNI, S. K. SOMAN and S. S. JOSHI, *J. Indian Chem. Soc.*, communicated.
3. S. V. KULKARNI, S. K. SOMAN and S. S. JOSHI, *J. Indian Chem. Soc.*, 1984, **61**, 684.
4. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longmans, London, 1961, p. 194.
5. R. W. GABALE and N. P. STROBEL, *J. Phys. Chem.*, 1965, **60**, 513.
6. R P. BHATNAGAR and N. C. JAIN, *J. Indian Chem. Soc.*, 1980, **57**, 168.
7. A. I. VOGEL, 'A Text Book of Quantitative Inorganic Analysis", Longmans, London, 1961, p. 629.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 781-783

On Glucosyl Thioureides. Part—IV. Synthesis of 3-Aryl-2,6-diphenylimino-4-*S*-tetra-*O*-acetyl-D-glucopyranosyl-5,6-dihydro-1,3,5-thiadiazine (Hydrochlorides)

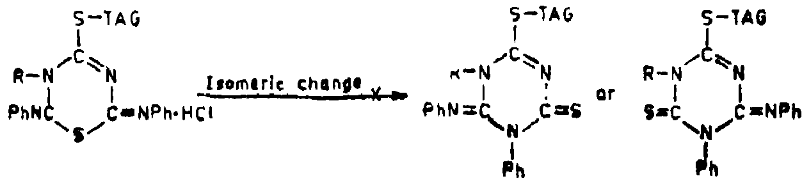
(Miss) I. D. BEDEKAR and M. G. PARANJPE

Department of Chemistry, Nagpur University, Nagpur-440 010

Manuscript received 12 July 1982, revised 10 April 1984, accepted 15 August 1984

Certain 3-aryl-2,6-diphenylimino-4-*S*-tetra-*O*-acetyl-D-glucopyranosyl-5,6-dihydro-1,3,5-thiadiazines (hydrochlorides) have been prepared by the interaction of phenyliso-cyanodichloride and 2-*S*-tetra-*O*-acetyl-D-glucopyranosyl-1-aryl-5-phenyl-2,4-isodithio-biurets. The identities of these products have been established on the basis of usual chemical transformations, ir, and polarimetry. All the attempts to isomerize these products into the related 1,3,5-triazines (IV or V) have been unfruitful.

RECENTLY, we have reported a procedure for the synthesis of 4-aryl-5-phenylimino-3-*S*-tetra-*O*-acetyl-D-glucopyranosyl-1,2,4-thiadiazolines[1]. In view of the importance of thioglucosides in medicinal chemistry, it appeared interesting to synthesize certain 1,3,5-triazines having tetra-*O*-acetyl-D-glucopyranosyl group. Therefore, interaction of 2-*S*-tetra-*O*-acetyl-D-glucopyranosyl-1-aryl-5-phenyl-2,4-isodithiobiurets and phenylisocyanodichloride have been undertaken with a view to synthesize 1,3,5-triazine derivatives.



III IV V

When the interaction of phenylisocyanodichloride has been carried out with 2-*S*-tetra-*O*-acetyl-D-glucopyranosyl-1,5-diphenyl-2,4-isodithiobiuret in boiling benzene medium for 3 h, evolution of hydrogen chloride was noticed. After reaction, benzene was distilled off. The residue when triturated several times with petroleum ether, was converted into a pale yellow solid. It was purified by precipitating it from its benzene solution with petroleum ether, m.p. 105°(d).

The product was acidic to litmus and gave effervescence with aqueous sodium bicarbonate. It was found non-desulphurisable when boiled with alkaline plumbite solution. It charred when heated with sulphuric acid. It afforded a picrate, m.p. 146°, when its ethanolic solution was treated with ethanolic picric acid. The product was found to have $[\alpha]_D^{31}$ +13.78° (c 1.6408 in chloroform)[a] ; ν_{max} 1595,

TABLE 1—SYNTHESIS OF 3-ARYL-2,6-DIPHENYLIMINO-4-*S*-TETRA-*O*-ACETYL-*D*-GLUCOPYRANOSYL-5,6-DIHYDRO-1,3,5-THIADIAZINES (HYDROCHLORIDES)

Sl. no.	2-*S*-Tetra-*O*-acetyl-D-glucopyranosyl-1-aryl-5-phenyl-2,4-isodithiobiurets (g)	3-Aryl-2,6-diphenylimino-4-*S*-tetra-*O*-acetyl-D-glucopyranosyl-5,6-dihydro-1,3,5-thiadiazines (hydrochloride) III m.p. (°C), yield (g)	Analysis % ; Found/(Calcd.) N	S	$[\alpha]_D^{31}$ in chloroform (c)	Picrate m.p. °C	N% ; Found/(Calcd.)
1.	-1-phenyl-,(6.1)	-3-phenyl-, IIIa 105 (d), 3.0	7.62 (7.42)	7.34 (8.48)	+ 13.78° (1.6408)	146	9.73 (10.35)
2.	-1-*o*-tolyl-,(6.3)	-3-*o*-tolyl-, IIIb 135 (d), 3.5	7.16 (7.28)	8.10 (8.32)	− 7.226° (1.855)	140	10.97 (10.20)
3.	-1-*m*-tolyl-,(6.3)	-3-*m*-tolyl-, IIIc 128 (d), 4.0	6.76 (7.28)	7.63 (8.32)	+ 35.83° (0.9703)	130	11.00 (10.20)
4.	-1-*p*-tolyl-,(6.3)	-3-*p*-tolyl-, IIId 125 (d), 3.8	6.89 (7.28)	7.93 (8.32)	+312.1°	136	9.68 (10.20)
5.	-1-*o*-Cl-phenyl-,(6.5)	Not isolated	—	—	—	—	—
6.	-1-*m*-Cl-phenyl-,(6.5)	-3-*m*-Cl-phenyl-, IIIf 115 (d), 4.2	6.68 (7.09)	7.32 (8.11)	+ 3.161° (1.07)	138	10.60 (9.98)

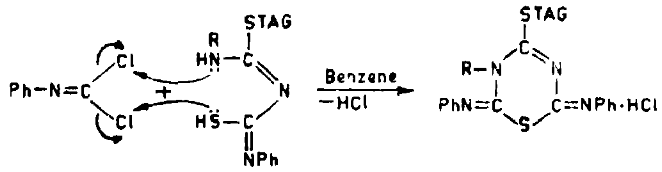
(N–C=N), 1625 (S–C=N), 685 (C–S–C) and 1750 cm^{-1} (C=O) (present as acetyl group in glucose residue)[3,4].

On the basis of the above facts it was quite evident that the reaction product with m.p. 105°(d) was a 1,3,5-thiadiazine (hydrochloride) for which structure 3-phenyl-2,6-diphenylimino-4-*S*-tetra-*O*-acetyl-D-glucopyranosyl-5,6-dihydro-1,3,5-thiadiazine (hydrochloride) (**IIIa**) has been assigned.

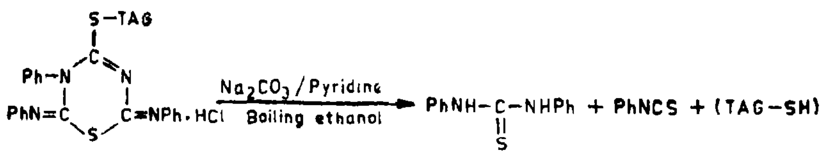
Attempts have been made also towards isomerization of the product with m.p. 105° (d), into the related 1,3,5-triazine (**IVa** or **Va**) by reacting it with (i) boiling ethanolic sodium carbonate and (ii) with ethanolic pyridine solutions. In both the cases product decomposed and 1,3-diphenylthiocarbamide, m.p. 154°, phenylisothiocyanate and thioglucoside have been detected from the decomposition products.

The interaction of phenylisocyanodichloride was also capable of extension to several other 2-*S*-tetra-*O*-acetyl-D-glucopyranosyl-1-aryl-5-phenyl-2,4-isodithiobiuretes (**IIb-IIf**). In all these cases the corresponding 1,3,5-thiadiazines (hydrochlorides) (**IIIb-IIIf**) only have been obtained (Table 1).

The mechanism of formation of **III** may be depicted as follows:



I II III



IIIa

where, R=(a) phenyl, (b) *o*-tolyl, (c) *m*-tolyl, (d) *p*-tolyl, (e) *o*-Cl-phenyl and (f) *m*-Cl-phenyl, TAG=Tetra-*O*-acetyl-D-glucopyranosyl.

tetra-*O*-acetyl-D-glucopyranosyl-1,5-diphenyl-2,4-isodithiobiuret (**II**) (0.01 *M*, 6.17 g in 40 ml). The mixture after shaking was refluxed over a boiling water bath for 3 h. During the reaction evolution of hydrogen chloride was noticed. Then benzene was distilled off. The resultant viscous residue was then triturated several times with petroleum ether, a pale yellow solid (**IIIa**) (3 g) was isolated. It was purified by precipitating it from its benzene solution with petroleum ether, m.p. 105° (d) (Found: C, 55.24, H, 4.52, N, 7.62, S, 7.84. $C_{35}H_{34}O_9N_4S_2$, HCl requires C, 55.65, H, 4.77, N, 7.42, S, 8.48%).

The other 3-aryl-2,6-diphenylimino-4-*S*-tetra-*O*-acetyl-D-glucopyranosyl-5,6-dihydro-1,3,5-thiadiazines (hydrochlorides) (**IIIb-IIIf**) have been prepared by the extension of reaction of phenylisocyanodichloride (**I**) to other 2-*S*-tetra-*O*-acetyl-D-glucopyranosyl-1-aryl-5-phenyl-2,4-isodithiobiuretes (**IIb-IIf**) (Table 1).

Attempts towards the isomerization of **IIIa** *to* **IVa**/**Va**: (a) *Reaction with ethanolic sodium carbonate*:

The product (5 g) was mixed with 5% aqueous ethanolic solution of sodium carbonate (30 ml) and the resultant clear solution was refluxed over a boiling water bath for 4 h. During heating, gradually, solution turned from yellow to dark brown in colour. The solvent ethanol was then distilled off and a viscous brown liquid was isolated. It had the characteristic odour of phenylisothiocyanate, which is confirmed by extracting it with petroleum ether followed by reaction with aniline, when 1,3-diphenylthiocarbamide[7], m.p. 152° was isolated.

The petroleum ether insoluble semi-solid mass, when treated with little ethanol afforded a solid, crystallised from aqueous ethanol, m.p. 152°. It was identified as 1,3-diphenylthiocarbamide on the basis of undepressed m.m.p. with authentic sample[7]. The ethanol solution responded to Molisch test indicating glucosyl compound.

Experimental

The required 2-*S*-tetra-*O*-acetyl-D-glucopyranosyl-1-aryl-5-phenyl-2,4-isodithiobiurets have been prepared as usual[5]. The phenylisocyanodichloride has been prepared by passing excess of chlorine gas into the chloroform solution of phenyl isothiocyanate[6].

3-Aryl-2,6-diphenylimino-4-S-tetra-O-acetyl-D-glucopyranosyl-5,6-dihydro-1,3,5-thiadiazines (hydrochlorides) (**III**):

Details of a typical experiment (where, aryl= phenyl) are as follows: A benzene solution of phenylisocyanodichloride (**I**) (0.01 *M*, 1.74 g in 20 ml) was mixed with a benzene suspension of 2-*S*-

(b) *Reaction with ethanolic pyridine :*

The product (5 g) was mixed with 5% ethanolic pyridine solution (50 ml) and the resultant clear solution was refluxed over a boiling water bath for 5 h. The solution gradually turned into a blackish brown in colour. After heating the solvent ethanol was distilled off. The viscous oily liquid was then washed with 5% aqueous hydrochloric acid to remove pyridine. The acid washed semi-solid had the odour of phenylisothiocyanate which was confirmed by extracting it with the help of petroleum ether and reacting the extract with aniline, when 1,3-diphenylthiocarbamide[7], m.p. 151° was isolated.

The petroleum ether insoluble semi-solid when treated with a little ethanol afforded shining plates, crystallised from aqueous ethanol, m.p. 152°. It was identified as 1,3-diphenylthiocarbamide on the basis of undepressed m.m.p. with the authentic sample[7]. The ethanol soluble portion responded to positive Molisch test indicating the presence of glucosyl compound.

Acknowledgement

One of the authors (I.D.B.) is grateful to U.G.C., New Delhi for a Teacher Fellowship and to Dr. K. N. Munshi, Head of the Department of Chemistry, Nagpur University for necessary facilities.

References

1. I. D. Bedekar, A. H. Lokhande and M. G. Paranjpe, *J. Indian Chem. Soc.*, 1984, **61**, 482.
2. "Physical Methods of Organic Chemistry", ed. Arnold Weissberger, 2nd ed., Interscience, New York, 1949, Part II.
3. R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds", John Wiley, New York, 1968.
4. N. B. Colthup, L. H. Daly and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1964.
5. I. D. Bedekar, A. R. Joshi and M. G. Paranjpe, *J. Indian Chem. Soc.*, 1981, **58**, 1015.
6. G. M. Dyson and T. Harington, *J. Chem. Soc.*, 1940, 191.
7. A. I. Vogel, "A Text-Book of Practical Organic Chemistry", Longmans Green, London, 1962.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 784-787

Potential Fungicides. Part—III. Synthesis and Evaluation of 5-Methyl-4-thiazolidinones and 5-Methyl-2,4-thiazolidindiones

RAM LAKHAN* and OM PRAKASH SINGH

Department of Chemistry, Banaras Hindu University, Varanasi-221 005

Manuscript received 17 June 1983, revised 16 March 1984, accepted 10 August 1984

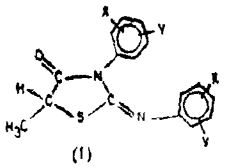
Several new 2-arylimino-3-aryl-5-methyl-4-thiazolidinones (1) and 3-aryl-5-methyl-2,4-thiazolidindiones (3) have been synthesised and screened for their antifungal activity against *Trichoderma viride* and *Curvularia lunata* at dilutions 1 : 1000 and 1 : 5000 by agar growth food poison technique. The activity was compared to that of a commercially used fungicide Cuman (80% Ziram) and it was found that 3 inhibit the growth of fungus colony more effectively in comparison to the standard. A couple of new 2-arylimino-3-aryl-5-methyl-4-thiazolidinone-1,1-dioxides (2) were also prepared by $KMnO_4$ oxidation of 1.

VERY diverse range of biological activities are associated with substituted 4-thiazolidinones[1] and 2,4-thiazolidindiones[2]. Some typical properties they exhibit are local anaesthetic[3], antibacterial[4], antifungal[5-8], hypnotic[9], anticonvulsant[10], anthelmintic[11], antiradiation[12] and cardiovascular effects[13]. Furthermore, 1,1-dioxides of 4-thiazolidinones exhibit a significant amoebicidal[14] and anticonvulsant activity[10].

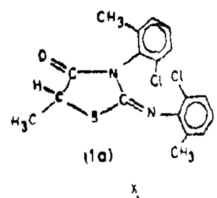
In consideration of such a versatile activity of 4-thiazolidinones, it was thought worthwhile to synthesise some new 2-(disubstituted)arylimino-3-(disubstituted)aryl-5-methyl-4-thiazolidinones (1), their 1,1-dioxides (2) and 3-(disubstituted)aryl-5-methyl-2,4-thiazolidindiones (3), and evaluate their antifungal activity.

The heterocyclic system (1) was synthesised by the interaction of symmetrical 1,3-bis-(disubstituted)-phenyl thioureas with equimolar amounts of 2-bromopropionic acid in presence 2 moles of anhydrous sodium acetate in absolute ethanol (Method A). Alternatively, they were also obtained by the condensation of equimolar quantities of symmetrical 1,3-bis-aryl thioureas with ethyl 2-bromopropionate in presence of 2 moles of pyridine (Method B). Wherever 4-thiazolidinones (1) were prepared by following the procedures *A* as well as *B*, the yields of products were practically the same (Table 1). The 4-thiazolidinones give characteristic ir bands at 1730 (m, C=O stretch), 1625 (s, C=N stretch), 1590m and 1500s (aromatic) cm^{-1}.

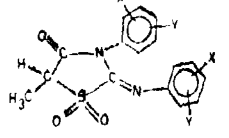
Oxidation of four typical 2-arylimino-3-aryl-4-thiazolidinones (1) with potassium permanganate in aqueous acetic acid led to the formation of the corresponding 2-arylimino-3-aryl-4-thiazolidinone-1,1-dioxides (2). Their ir spectra show bands at 1310m and 1135m cm^{-1}, which are characteristic of sulphones, in addition to the usual bands.



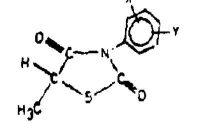
(1)



(1a)



(2)



(3)

All the 4-thiazolidinones except **1a** were hydrolysed with strong HCl by heating under reflux in ethanolic or acetic acid medium for 6~36 h. Hydrolysis of **1** under such conditions partially cleaved the molecule at position 2 to give the corresponding aniline and 3-aryl-5-methyl-2,4-thiazolidindione (**3**) in high yields. The ease with which the hydrolysis takes place, monitored in terms of the reaction time, has been rationalised to throw some light on the mechanism of hydrolysis. The 4-thiazolidinones, that were subjected to hydrolysis, may be broadly classified into three categories.

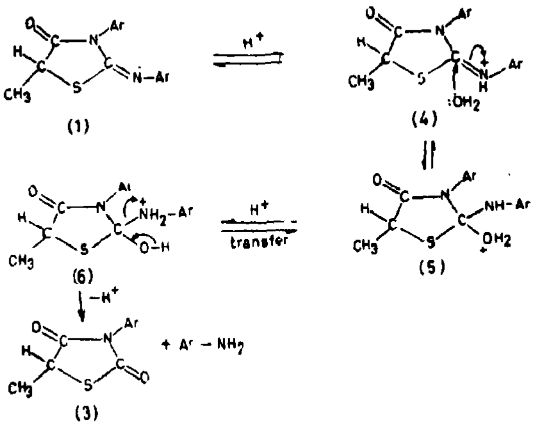
(i) Compounds (**1h**, **1i** and **1d**) having either a *o*- or *p*-methoxy substituent or a *p*-methyl in the phenyl ring of 2-arylimino group, require a relatively short time of 6~10 h to get hydrolysed to the related **3**.

(ii) Compounds (e.g. **1b** and **1g**) having either a *o*−CH_3 or *o*−Cl substituent in the phenyl ring at position 2, require 24~36 h to undergo hydrolysis to the 2,4-thiazolidindione (**3**).

(iii) Compound **1a** in which both the *o*-positions of phenyl ring are substituted by CH_3 and Cl groups,

failed to undergo hydrolysis under similar conditions even after refluxing for a longer period (48 h). Moreover, it did not hydrolyse in boiling glycerol also by heating for 8 h at 270°.

These observations have prompted to propose a mechanism for the hydrolysis of 4-thiazolidinones (Scheme 1).



Scheme 1

The reaction involves reversible protonation of (1) at the imino nitrogen thereby making carbon at position 2 susceptible to nucleophilic attack by water in a reversible process forming the intermediate (5). The latter by a simple proton transfer gives (6) which eliminates a molecule of substituted aniline to give (3) in a non-reversible process. The formation of intermediates (4) and (6) is apparently favoured by electron-releasing substituents when present at the *p*-position (*e.g.* methoxy or methyl) and that explains the behaviour of **1i** and **1d** towards quick hydrolysis. 4-Thiazolidinones placed in category (ii) exert a combination of steric and electronic effect (inductive, hyperconjugative, *etc.*) of substituents to a varying degree when subjected to hydrolysis. On the other hand, the steric and polar effect of substituents in **1a** was so great that it could not be hydrolysed to corresponding **3a** even under drastic conditions.

Experimental

Melting points were observed with a Gallenkamp apparatus and are uncorrected. Elemental analyses (C, H and N) were carried on a Coleman Analyser. The ir spectra (nujol) were recorded on a Perkin-Elmer 720 grating spectrophotometer, while nmr on a Varian-A60D instrument at the probe temperature (45°) as CCl_4 or $CDCl_3$ solutions using TMS as an internal reference. The purity of compounds was checked routinely by tlc using silica gel G (E. Merck).

1,3-Bis-aryl thioureas : These were prepared by modifying the method of Fry[15]. A mixture of 2-methyl-3-chloroaniline (14.1 g, 0.10 mol), iodine (12.7 g, 0.05 mol), pyridine (15.8 g, 0.20 mol) and carbon disulphide (150 ml, 2.5 mol) was heated under reflux on a water bath until the colour of iodine disappeared. The product was steam distilled to remove traces of carbon disulphide and pyridine. The residue was filtered under suction and washed with water to remove pyridinium iodide. It was dried and crystallised from ethanol to give 1,3-bis-(2-methyl-3-chloro)phenyl thiourea (85%), m.p. 190° (Found : C, 55.3 ; H, 4.2 ; N, 8.6 ; S, 10.0. $C_{15}H_{14}Cl_2N_2S$ calcd. C, 55.4 ; H, 4.3 ; N, 8.6 ; S, 9.9%) ; ν_{max} (nujol) 3390m, 3200m (N – H stretching), 1590m, 1540s cm^{-1} (aromatic ring).

2-(2'-Methyl-3'-chloro)phenylimino-3-(2'-methyl-3'-chloro)phenyl-5-methyl-4-thiazolidinone (**1c**) : Method A. A mixture of 1,3-bis-(2-methyl-3-chloro)phenyl thiourea (6.5 g, 0.02 mol), 2-bromopropionic acid (3.4 g, 0.022 mol), anhydrous sodium acetate (4.0 g, 0.04 mol) and absolute ethanol (35 ml) was refluxed on a water bath for 8 h with occasional shaking. After completion of the reaction ethanol was distilled off and the gummy product washed with hot water which solidified on keeping overnight in contact with ice-water. It was filtered, dried and crystallised from ethanol to form colourless crystals (48%), m.p. 97° (Found : C, 57.3 ; H, 4.0 ; N, 7.1 ; S, 8.8. $C_{18}H_{16}Cl_2N_2OS$ calcd. C, 57.0 ; H, 4.2 ; N, 7.4 ; S, 8.4%) ; ν_{max} (nujol) 1730m, 1625s, 1590m cm^{-1} ; $\delta(CDCl_3)$ 6.63-7.60 (m, 6H), 4.21 (q, *J* 7Hz, 1H), 1.71 (d, *J* 7Hz, 3H), 2.08 (s, 3H), 2.25 (s, 3H).

2-(2'-Methoxy-5'-chloro)phenylimino-3-(2'-methoxy-5'-chloro)phenyl-5-methyl-4-thiazolidinone (**1h**) : Method B. A mixture of 1,3-bis-(2'-methoxy-5'-chloro)phenyl thiourea (7.0 g, 0.02 mol), ethyl 2-bromopropionate (3.8 g, 0.021 mol), pyridine (1.6 g, 0.02 mol) and absolute ethanol (35 ml) was heated under reflux on a water bath for 8 h with occasional shaking. Then ethanol and pyridine were removed by distillation and the product was washed with hot water. It solidified on keeping in contact with ice. It was filtered, dried and crystallised from ethanol to afford colourless crystals (60%) m.p. 191° (Found : C, 52.5 ; H, 3.9 ; N, 6.9 ; S, 7.7. $C_{18}H_{16}Cl_2N_2O_3S$ calcd. C, 52.6 ; H, 3.9 ; N, 6.8 ; S, 7.8%) ; ν_{max} (nujol) 1730m, 1630s, 1580m, 1500s cm^{-1} ; $\delta(CDCl_3)$ 6.80-7.60 (m, 6H), 4.20 (q, *J* 7Hz, 1H), 1.78 (d, *J* 7Hz, 3H), 3.85 (m, 6H).

Other 2-arylimino-3-aryl-5-methyl-4-thiazolidinones (**1**) were prepared by following method A or B. Their characterization data are recorded in Table 1.

2-(2'-Methyl-5'-chloro)phenylimino-3-(2'-methyl-5'-chloro)phenyl-5-methyl-4-thiazolidinone-1,1-dioxide (**2b**) : A solution of 1.0 g potassium permanganate in 30 ml water was added dropwise with stirring to 2-(2'-methyl-5'-chloro)phenylimino-3-(2'-methyl-5'-chloro)phenyl-4-thiazolidinone (0.6 g) dissolved in 20 ml glacial acetic acid. The addition was complete in 30 min. Aqueous sodium bisulphite was then added to the reaction mixture until it was colourless. The tan coloured precipitate was filtered, dried and crystallised from ethanol, (70%), m.p. 235°

TABLE 1—2-ARYLIMINO-3-ARYL-5-METHYL-4-THIAZOLIDINONES (1)* AND 2-ARYLIMINO-3-ARYL-5-METHYL-4-THIAZOLIDINONE-1,1-DIOXIDES (2)*

Sl no.	Substituents X	Substituents Y	Method	Yield %	m.p. °C
1a	2-CH_3	6-Cl	A/B	80	144
1b	2-CH_3	5-Cl	A/B	70	124
1c	2-CH_3	3-Cl	A	48	97
1d	4-CH_3	3-Cl	A/B	45	77
1e	2-Cl	3-Cl	A	48	123
1f	2-Cl	4-Cl	A	55	128
1g	2-Cl	5-Cl	A/B	82	164
1h	2-OCH_3	5-Cl	A/B	60	191
1i	4-OCH_3	3-Cl	A	78	76
2a	2-CH_3	6-Cl	—	70	147
2b	2-CH_3	5-Cl	—	70	235
2g	2-Cl	5-Cl	—	60	159
2h	2-OCH_3	5-Cl	—	70	183

* Spectral data (nmr and ir) in accord with their structures ; satisfactory analyses for N and S.

(Found : C, 52.5 ; H, 4.1 ; N, 7.2 ; S, 7.7. $C_{18}H_{16}Cl_2N_2O_3S$ calcd. C, 52.6 ; H, 3.9 ; N, 6.8 ; S, 7.8%) ; ν_{max} (nujol) 1745m, 1720m, 1685s, 1645m, 1595m, 1310m, 1135m cm^{-1}.

Similarly other 2-arylimino-3-aryl-5-methyl-4-thiazolidinone-1,1-dioxides (**2**) were prepared. Their yield, melting point and analytical data are listed in Table 1.

Hydrolysis of 2-(2′-methyl-3′-chloro)phenylimino-3-(2′-methyl-3′-chloro)phenyl-5-methyl-4-thiazolidinone (**1c**) : *Formation of 3-(2′-methyl-3′-chloro)phenyl-5-methyl-2,4-thiazolidindione* (**3c**) : To a solution of 1.0 g 2-(2′-methyl-3′-chloro)phenylimino-3-(2′-methyl-3′-chloro)phenyl-5-methyl-4-thiazolidinone in 20 ml ethanol, 5 ml strong HCl was added and the mixture refluxed on a water bath for 36 h. Ethanol was then distilled off and the product was poured into water and filtered. The residue was washed several times with water, dried and crystallised from ethanol to give 3-(2′-methyl-3′-chloro)phenyl-5-methyl-2,4-thiazolidindione (55%), m.p. 128° (Found : C, 46.1 ; H, 3.5 ; N, 6.2 ; S, 10.8. $C_{11}H_{10}ClNO_2S$ calcd. C, 45.9 ; H, 3.5 ; N, 6.1 ; S, 11.1%) ; IR ν_{max} (nujol) 1750m, 1680s, 1580m, 1500m cm^{-1} ; $\delta(CDCl_3)$ 7.03-7.58 (m, 3H), 4.30 (q, J 7Hz, 1H), 1.75 (d, J 7Hz, 3H), 2.13 (s, 3H).

All the 3-aryl-5-methyl-2,4-thiazolidindiones (**3**) reported in Table 2 were prepared from the hydrolytic cleavage of **1** in ethanolic HCl medium except **3e** and **3g**. The latter were obtained by hydrolysis of **1e** and **1g**, respectively, in acetic acid with strong HCl. The time required for the hydrolysis of **1** to give the corresponding **3**, and the yield, melting point, and analytical data of 2,4-thiazolidindiones are recorded in Table 2.

Experiments under similar conditions failed to hydrolyse 2-(2′-methyl-6′-chloro)phenylimino-3-(2′-methyl-6′-chloro)phenyl-5-methyl-4-thiazolidinone (**1a**), and that 3-(2′-methyl-6′-chloro)phenyl-5-methyl-2,4-thiazolidindione could not be prepared. Hydrolysis of **1a** with strong HCl did not occur even in a higher boiling alcohol, glycerol, at a temperature 270° by heating for 8 h.

TABLE 2—3-(DISUBSTITUTED)ARYL-5-METHYL-2,4-THIAZOLIDINDIONES (3)*

Sl. no.	Substituents X	Substituents Y	Reaction time h.	Yield %	M.p. °C
3b	2-CH_3	5-Cl	24	70	75
3c	2-CH_3	3-Cl	36	55	128
3d	4-CH_3	3-Cl	10	60	112
3e	2-Cl	3-Cl	36	70	137
3f	2-Cl	4-Cl	36	75	76
3g	2-Cl	5-Cl	36	50	119
3h	2-OCH_3	5-Cl	6	75	110
3i	4-OCH_3	3-Cl	6	68	146

* Footnote as in Table 1.

Fungicidal activity screening : All the nine 4-thiazolidinones (**1**) and seven out of eight 2,4-thiazolidindiones (**3**) except **3f** were evaluated for their antifungal activity against two typical agricultural fungi *Trichoderma viride* and *Curvularia lunata* by agar growth food poison technique at dilutions of 1 : 1000 and 1 : 5000 (Table 3).

TABLE 3—ANTIFUNGAL ACTIVITY OF 2-ARYLIMINO-3-ARYL-5-METHYL-4-THIAZOLIDINONES (1) AND 3-ARYL-5-METHYL-2,4-THIAZOLIDINDIONES (3)

Medium, Czapek's agar ; Time, 4 days ; Temp , 25 ± 1°

Sl. no.	% Inhibition of *Trichoderma viride* at dilutions		% Inhibition of *Curvularia lunata* at dilutions	
	1 : 1000	1 : 5000	1 : 1000	1 : 5000
1a	29	21	50	40
1b	39	15	24	17
1c	35	19	63	28
1d	39	22	47	32
1e	55	34	60	10
1f	43	34	54	41
1g	21	19	50	17
1h	51	43	50	21
1i	41	18	60	30
3b	100	78	100	73
3c	100	80	84	77
3d	100	71	100	73
3e	86	46	84	44
3g	88	58	80	47
3h	82	60	84	63
3i	100	60	84	57
Cuman*	27	16	57	50
	(34)	(20)	(71)	(62)

* Values in parentheses denote the extrapolated percentage inhibition of the standard fungicide for 100% Ziram content.

Results and Discussion

It is concluded from the screening results that 2,4-thiazolidindiones (**3**) are more active fungicides against both the fungi in comparison to a standard commercial fungicide Cuman (80% Ziram). On the other hand, 4-thiazolidinones (**1**) inhibit fungus growth more or less to the same extent as Cuman.

For a given set of substituents, the 2,4-thiazolidindiones (**3**) containing only one aryl group are

more fungicidal than the corresponding 4-thiazolidinones (**1**) containing two aryl groups. This indicates that the fungicidal effect is basically due to the presence of a thiazolidinone nucleus and that the substituents present in the aryl group only modify the activity to some extent. A vacant 2-position in **3** presumably makes the active site more freely available for attack on the fungus and thereby it checks fungal growth to a greater extent. Among the tested compounds **3b**, **3c** and **3d** are found to be the most effective.

Acknowledgement

We express our thanks to Professor B. M. Shukla, Head of the Department of Chemistry, Professor R. S. Dwivedi, Head of the Mycological Laboratory, Centre of Advanced Studies in Botany, and Dr. P. N. Bhargava, Retired Professor of Organic Chemistry, Banaras Hindu University for providing the necessary facilities and useful discussions. Thanks are also due to C.S.I.R., New Delhi for the award of a Junior Research Fellowship to one of the authors (O.P.S.).

References

1. P. N. Bhargava, S. Prakash and R. Lakhan, *Indian J. Chem., Sect. B*, 1981, **20**, 927 (Part I); R. Lakhan, *Agric. Biol. Chem.*, 1982, **46**, 557 (Part II).
2. G. R. Newkome and A. Nayak, *Adv. Heterocycl. Chem.*, 1979, **25**, 88.
3. A. R. Surrey, *J. Am. Chem. Soc.*, 1949, **71**, 3105, 3354; P. R. Singh, *Indian J. Chem.*, 1963, **1**, 100; P. N. Bhargava and M. R. Chaurasia, *J. Pharm. Sci.*, 1969, **58**, 896; *Indian J. Pharm.*, 1968, **30**, 125.
4. M. J. Mousseron, U. S. Patent 3678041, 1972 (*Chem. Abstr.*, 1972, **77**, 114388).
5. M. K. Rout and G. N. Mohapatra, *J. Am. Chem. Soc.*, 1955, 77, 2427.
6. K. S. L. Srivastava, *Curr. Sci.*, 1968, **37**, 315; *Indian J. Appl. Chem.*, 1969, **32**, 369.
7. G. Matolcsy, B. Bordas and M. Hamran, *Acta Phytopathol.*, 1969, **4**, 345 (*Chem. Abstr.*, 1970, **73**, 86843).
8. P. N. Bhargava and I. C. Tiwari, *Curr. Sci.*, 1973, **42**, 717; R. Shyam and I. C. Tiwari, *Agric. Biol. Chem.*, 1975, **39**, 715.
9. W. J. Doran and H. A. Shonle, *J. Org. Chem.*, 1938, 3, 193.
10. H. D. Troutman and L. M. Long, *J. Am. Chem. Soc.*, 1948, **70**, 3436.
11. S. E. Leland, J. M. Kling and L. J. Wallace, *J. Parasitol.*, 1967, **53**, 20.
12. T. Yu. Il'yuchenok, L. M. Frigidova and K. S. Shadurskii, *Farmakol. Toksikol.*, 1980, 43, 725 (*Chem. Abstr.*, 1981, **94**, 57954).
13. S. Nagar, H. H. Singh, J. N. Sinha and S. S. Parmar, *J. Med. Chem.*, 1973, **16**, 178.
14. A. R. Surrey and R. A. Cutler, *J. Am. Chem. Soc.*, 1954, **76**, 578.
15. H. S. Fry, *J. Am. Chem. Soc.*, 1913, **35**, 1539.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 788-789

Studies on Sulphonylhydrazones : Preparation and Antimicrobial Activity of Arylsulphonyl-(4-substituted)-aceto/propiophenonehydrazones

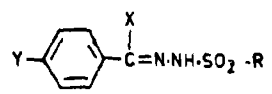
D. J. BHATT, G. C. KAMDAR and A. R. PARIKH

Department of Chemistry, Saurashtra University, Rajkot-360 005

Manuscript received 25 July 1983, revised 21 April 1984, accepted 15 August 1984

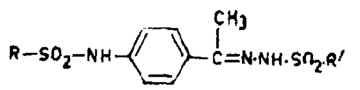
Some new arylsulphonylhydrazones have been prepared by condensation of p-chloroacetophenone, p-methylpropiophenone and p-bromopropiophenone and 4-arylsulphonamidoacetophenone with different arylsulphonylhydrazines. The products were tested for antimicrobial activity. The constitution was supported by ir spectra.

SULPHONYLHYDRAZINE derivatives possess wide therapeutic activity, *viz.* antibacterial[1], fungicidal[2] and antituberculostatic[3] activity. Sulphonamides[4] showed antibacterial, anticancer, anticonvulsant, antimalarial and antifungal activities. *p*-Amino acetophenone has the same bactericidal effect as sulphonamides[5]. With a view to get better therapeutic agents, we have prepared different arylsulphonyl-(4-chloro/bromo/methyl)-aceto/propiophenonehydrazones (I) by the condensation of *p*-chloroacetophenone, *p*-methyl propiophenone and *p*-bromopropiophenone with different sulphonylhydrazines. The sulphonylhydrazines were synthesised by condensing different arylsulphonylchloride and hydrazine hydrate[6].



(I)

Y = Cl, CH_3, Br ; X = CH_3, C_2H_5 ; R = Aryl



(II)

R = Aryl

Arylsulphonylhydrazones of the type II were also prepared by condensing 4-arylsulphonamido acetophenone with different arylsulphonyl hydrazines. The constitution of the products were supported by ir spectra[7]. The products were screened for antibacterial activity.

The ir spectra (KBr) of phenylsulphonyl-4-bromopropiophenone hydrazone (I) showed bands at 3220 (NH stretching) and 1320 cm^{-1} (SO_2), and those of phenylsulphonyl-(4-sulphonamido)-acetophenonehydrazone showed bands at 3220 (NH stretching), 1320 (S–O) and 1160 cm^{-1} (SO_2NH).

Experimental

Preparation of arylsulphonyl-(4-chloroacetophenonehydrazone) : The phenylsulphonylhydrazine (0.01 mol) was dissolved in hot methanol (25 ml) containing a little water. *p*-Chloroacetophenone (0.01 mol) was then added dropwise with stirring. The crystals were separated from the reaction mixture after 2 h at room temperature. The product was filtered and crystallised from methanol. Similarly other products were prepared by condensing different arylsulphonylhydrazines with *p*-bromoacetophenone, *p*-methylacetophenone, *p*-toluenesulphonamidoacetophenone and *p*-benzenesulphonamidoacetophenone.

Antibacterial activity : The compounds were tested for antibacterial activity against *S. aureus* and *E. coli* by cup-plate method[8] using ethanol as solvent. When R = phenyl and *p*-chlorophenyl, X = ethyl, Y = bromo of type I, they were highly active (zone of inhibition – 40-44 mm) against *S. aureus* ; and when R = *p*-anisyl, phenyl and *p*-bromophenyl, X = ethyl, Y – bromomethyl of type I they were highly active (zone of inhibition – 30 mm) against *E. coli*. When R = *p*-chlorophenyl, R′ = *p*-chlorophenyl and *p*-tolyl of type II they were highly active (zone of inhibition = 40 mm) against *S. aureus*. Other products of type I and II were moderately active against *S. aureus* and *E. coli* (zone of inhibition = 10 to 30 mm).

TABLE 1—ARYLSULPHONYL-(4-SUBSTITUTED)-ACETO/PROPIOPHENONE HYDRAZONES

Sl. no.	R	X	Y	M.p. °C	Yield %	N% Found/ (Calcd.)
1.	Phenyl	Methyl	Chloro	171-73	60	9.0 (9.08)
2.	p-Chlorophenyl	Methyl	Chloro	166-67	71	8.2 (8.16)
3.	p-Tolyl	Methyl	Chloro	155-56	70	8.4 (8.68)
4.	p-Bromophenyl	Methyl	Chloro	140-42	68	7.0 (7.23)

(Table 1 contd.)

5.	Acetamidophenyl	Methyl	Chloro	162-63	62	11.20 (11.49)
6.	*o*-Hydroxyphenyl	Methyl	Chloro	180-82	72	8.50 (8.63)
7.	Anisyl	Methyl	Chloro	132-34	74	8.0 (8.27)
8.	Phenyl	Ethyl	Bromo	167-69	65	7.75 (7.63)
9.	*p*-Chlorophenyl	Ethyl	Bromo	145-47	64	6.8 (6.97)
10.	*p*-Tolyl	Ethyl	Bromo	166-68	66	7.5 (7.34)
11.	*p*-Bromophenyl	Ethyl	Bromo	144-46	68	6.35 (6.27)
12.	Acetamidophenyl	Ethyl	Bromo	162-64	58	9.8 (9.9)
13.	*o*-Hydroxyphenyl	Ethyl	Bromo	195-96	63	7.5 (7.31)
14.	Anisyl	Ethyl	Bromo	130-32	61	7.15 (7.05)
15.	Phenyl	Ethyl	Methyl	172-74	70	9.3 (9.27)
16.	*p*-Chlorophenyl	Ethyl	Methyl	166-68	72	9.45 (8.32)
17.	*p*-Tolyl	Ethyl	Methyl	155-57	71	8.95 (8.85)
18.	*p*-Bromophenyl	Ethyl	Methyl	140-42	72	7.52 (7.34)
19.	Acetamidophenyl	Ethyl	Methyl	162-63	70	11.78 (11.69)
20.	*o*-Hydroxyphenyl	Ethyl	Methyl	80-82	64	8.70 (8.8)
21.	*p*-Tolyl	Ethyl	Methyl	132-34	64	8.40 (8.86)

Compd. no. 1 gave satisfactory C, H analyses ; all compounds gave satisfactory N analyses.

TABLE 2—ARYLSULPHONYL-(4-SULPHONAMIDO)-ACETOPHENONE HYDRAZONES

Sl. no.	R	R′	M.p. °C	Yield %	N% Found/ (Calcd.)
1.	Phenyl	Phenyl	168-69	82	9.8 (9.79)
2.	Phenyl	Bromophenyl	180-81	73	8.8 (8.26)
3.	Phenyl	*p*-Chlorophenyl	110-11	71	9.10 (9.06)
4.	Phenyl	*p*-Tolyl	130-32	81	9.5 (9.48)
5.	Phenyl	Naphthyl	105-7	67	8.8 (8.77)
6.	Phenyl	*m*-Carboxyphenyl	152-55	80	8.7 (8.88)
7.	Phenyl	2-Hydroxy-3-Carboxyphenyl	122-24	80	8.6 (8.58)
8.	*p*-Tolyl	Phenyl	140-42	86	8.5 (9.48)
9.	*p*-Tolyl	Bromophenyl	149-51	80	8.0 (8.04)
10.	*p*-Tolyl	*p*-Chlorophenyl	180-82	77	8.9 (8.79)
11.	*p*-Tolyl	*p*-Tolyl	95-97	76	9.25 (9.19)
12.	*p*-Tolyl	Naphthyl	152-53	73	8.84 (8.52)
13.	*p*-Tolyl	*m*-Carboxyphenyl	145-46	81	8.8 (8.62)
14.	*p*-Tolyl	2-Hydroxy-3-caraboxyphenyl	130-32	83	8.20 (8.34)
15.	*p*-Chlorophenyl	Phenyl	146-48	85	9.0 (9.06)
16.	*p*-Chlorophenyl	Bromophenyl	120-22	81	7.6 (7.74)
17.	*p*-Chlorophenyl	*p*-Chlorophenyl	102-04	82	8.75 (8.43)
18.	*p*-Chlorophenyl	*p*-Tolyl	162-64	77	8.9 (8.80)
19.	*p*-Chlorophenyl	Naphthyl	160-61	79	8.5 (8.18)
20.	*p*-Chlorophenyl	*m*-Carboxyphenyl	108-10	81	8.3 (8.5)
21.	*p*-Chlorophenyl	2-Hydroxy-3-carboxyphenyl	120-21	81	8.00 (8.02)

Compd. no. 1 gave satisfactory C, H analyses ; all compounds gave satisfactory N analysis.

Acknowledgement

Authors are thankful to Saurashtra University for providing facilities.

References

1. T. RINDER SPACHER and B. PRUS, *Helv. Chim. Acta*, 1958, **41**, 22.
2. E. DEGENER, Brit. Pat., 1 085 476 1967.
3. T. S. GARDENAV, *J. Org. Chem.*, 1961, **26**, 1514.
4. R. S. MCCOUTCHOON, *Pharm. Index*, 1965, **7**, 413.
5. H. WILLSTAEDT, *Suenst. Chem. Tid.*, 1944, **56**, 267.
6. A. A. MUNSHI, N. M. SHAH and J. P. TRIVEDI, *Indian J. Chem.*, 1963, **1**, 311.
7. R. J. W. CREMLYN, *J. Chem. Soc.*, 1964, 6248.
8. S. P. HIREMUTH, M. G. PUROHIT and M. SIRSI, *Karnatak Univ. J. Sci.*, 1974, **29**, 208.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 790-791

Preparation and Antimicrobial Activity of *p,p'*-[Bis-(4-aryl-3-chloro-2-azetidinon-1-yl)]-Diphenylsulphones and Di-*m*-tolyl

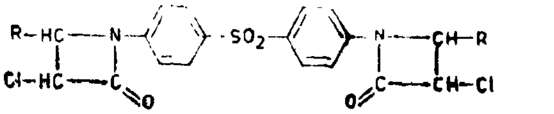
G. C. KAMDAR, D. J. BHATT and A. R. PARIKH

Department of Chemistry, Saurashtra University, Rajkot-360 005

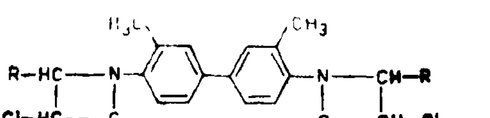
Manuscript received 25 July 1983, revised 21 April 1984, accepted 15 August 1984

Some new *p,p'*-[bis-(4-aryl-3-chloro-2-azetidinon-1-yl)]-diphenylsulphones and di-*m*-tolyl have been prepared. The constitution of the products was supported by ir spectra. The products were screened for antibacterial activity.

β-Lactum derivatives are most widely prescribed antibiotics in medicine[1]. 2-Azetidinone derivatives possess wide therapeutic activity, *viz.* sedative, hypnotic, anticonvulsant[2], herbicidal[3] and antibacterial[4]. *p,p'*-Diaminodiphenylsulphone possesses antibacterial[5] and antimalarial activity[6]. *o*-Tolidine derivatives also show bacteriostatic[7] and antifungal[8] activity. With a view to prepare better therapeutic agents, we have prepared *p,p'*-[bis-(4-aryl-3-chloro-2-azetidinon-1-yl)]-diphenylsulphone and di-*m*-tolyl by the condensation of chloroacetylchloride with Schiff bases[9,10] obtained from different aldehydes with *p,p'*-diaminodiphenylsulphone and *o*-tolidine. The constitution of the product was supported by ir spectra[11]. The ir spectra (KBr) of *p,p'*-[bis-(4-phenyl-3-chloro-2-azetidinon-1-yl)]-diphenylsulphone **I** showed bands at 1150 ($-SO_2-$), 1710 (C=O of *β*-lactum) and 750 cm^{-1} (C–Cl stretch). The spectra (KBr) of *p,p'*-[bis-(4-phenyl-3-chloro-2-azetidinon-1-yl)]-di-*m*-tolyl (**II**) showed bands at 1730 (C=O *β*-lactum) and 750 (C–Cl stretch). The products were screened for antimicrobial activity.



(I)



(II)

R = Aryl

Experimental

Preparation of p,p'-*[bis-(4-phenyl-3-chloro-2-azetidinon-1-yl)]-diphenylsulphone :* To well stirred solution of *p,p'*-bis-(benzalaminophenyl)-sulphone (0.01 mol) and triethylamine (0.02 mol) in dry dioxan (50 ml) was added monochloroacetylchloride (0.02 mol) dropwise at room temperature and the mixture was stirred for 5 h and left at room temperature for three days. The precipitate of triethylamine hydrochloride was filtered and washed with dioxane. The filtrate was treated with dried magnesium sulphate and the product was crystallised from ethanol to yield **I** (Found : C, 62.41 ; H, 3.85 ; N, 4.81 ; Cl, 12.35. $C_{30}H_{22}Cl_2N_2O_4S$ required C, 62.39 ; H, 3.81 ; N, 4.85 ; Cl, 12.30%). Similarly other Schiff bases from *o*-tolidine were condensed with monochloroacetyl chloride to get azetidinones of type **II**.

Antibacterial activity : The compounds were tested for antibacterial activity against *S. aureus* and *E. coli* by disk method[12] using ethanol as a solvent at a concentration of 10 mg ml^{-1}. The test solution containing 0.5 mg was used. From the experimental data it was observed that all compounds showed good activity against *S. aureus* and *E. coli*. The antibacterial activity is not better as compared to the well known antibiotics.

TABLE 1—PHYSICAL CONSTANTS OF *p,p'*-BIS-(4-ARYL-3-CHLORO-2-AZETIDINON-2-YL)-DIPHENYLSULPHONES (I)*

Sl. no.	R	M.p. °C	Yield %	Diameter of zone of inhibition mm	
				S. aureus 24 h	*E. coli* 24 h
1.	Phenyl	193	79	20	21
2.	*o*-Hydroxyphenyl	137	55	23	22
3.	*m*-Hydroxyphenyl	126	61	27	20
4.	*p*-Hydroxyphenyl	145	69	21	19
5.	3-Bromo-2-hydroxyphenyl	140	71	24	20
6.	3,5-Dibromo-2-hydroxyphenyl	135	85	24	19
7.	4-Hydroxy-3-methoxyphenyl	155	76	20	20
8.	*o*-Chlorophenyl	168	69	24	20
9.	*p*-Chlorophenyl	161	77	25	27
10.	α-Furfuryl	180	79	27	24

* All compounds gave satisfactory N analysis.

TABLE 2—PHYSICAL CONSTANTS OF *p,p'*-BIS-(4-ARYL-3-CHLORO-2-AZETIDINON-1-YL)-DI-*m*-TOLYL (II)*

Sl. no.	R	M.p. °C	Yield %	Diameter of zone of inhibition mm	
				S. aureus 24 h	*E. coli* 24 h
1.	Phenyl	265	81	28	24
2	o-Hydroxyphenyl	268	65	34	30
3.	*m*-Hydroxyphonyl	275	72	35	29
4.	*p*-Hydroxyphenyl	284	69	36	31
5.	3-Bromo-2-hydroxyphenyl	258	76	42	38
6.	3,5-Dibromo-2-hydroxyphenyl	209	85	44	41
7.	4-Hydroxy-3-methoxyphenyl	250	61	43	30
8.	*o*-Chlorophenyl	268	55	44	31
9.	*p*-Anisyl	265	64	44	30
10.	α-Furfuryl	275	71	41	21

* All compounds gave satisfactory N analysis.

Acknowledgement

The authors are thankful to Saurashtra University for providing facilities and also to U.G.C. and C.S.I.R., New Delhi for awarding Junior Research Fellowship to two of them (G.C.K. and D.J.B.).

References

1. T. KEMIYA, *Spec. Publ. Chem. Soc.*, 1977, 28.
2. G. MAFFI, *France* (*Pania*), *Ed. Sci.*, 1959, **14**, 76.
3. R. D. HOTZ and D. J. KRENZER, U. S. Pat., 3,9558, 974.
4. A. K. BOSE, M. S. MANNAN, J. C. KAPUR, S. D. SHARMA, *J. Med. Chem.*, 1974, **17**, 541.
5. NORTHEY, "The Sulphonemido and Allied Compounds", 1948, pp. 106, 411.
6. ARCHIBALD and C. M. ROSE, *J. Trop. Med. Hyg.*, 1960, **25**, 63.
7. K. KRAFT, *Pharmazie.*, 1950, **5**, 257.
8. G. J. HORSFALL and S. RICH, *Trans N. Y. Acad. Sci.*, 1955, **18**, 69.
9. K. J. MEHTA, Ph. D. Thesis, Saurashtra University, 1979.
10. U. H. PANDYA, Ph. D. Thesis, Saurashtra University, 1980.
11. J. C. SHEEHAN and A. K. BOSE, *J. Am. Chem. Soc.*, 1950, 72, 5158.
12. A. W. BAUER and W. M. M. KIRBY, *Am. J. Clin. Pathol.*, 1966, **45**, 493.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 792-793

Volatile Constituents of *Hypericum elodeoides* Chois

D. K. MATHELA and C. S. MATHELA*

Department of Chemistry, Kumaun University, Nainital-263 002

and

VASU DEV

California State Polytechnic University, Pomona, California-91768

Manuscript received 29 September 1983, revised 23 April 1984, accepted 10 August 1984

The essential oil of *Hypericum elodeoides* Chois (aerial part) has been found to contain nonane, four mono- and eight sesqui-terpene hydrocarbons, two mono- and five sesqui-terpene alcohols, and 7-hydroxycalamenene.

HYPERICUM elodeoides Chois. (Hypericaceae) is a perennial herb growing in tropical Himalayan forest. No work has been reported on the composition of the essential oil of this plant. The *Hypericum* species are frequently used as anthelmintic and as a remedy for dog-bite and bee-sting, and their seeds as diuretic and antispasmodic[1]. The present paper describes the characterization of 21 compounds in the essential oil of this species.

Experimental

The plants were collected from Bhowali (Nainital) in the month of September. The essential oil from the aerial part of *H. elodeoides* was extracted by steam distillation using a copper still fitted with spiral condenser and taken in petroleum ether (b.p. 60-80°). It was dried over anhydrous sodium sulphate, filtered and the essential oil was concentrated by distilling off the solvent under reduced pressure. The physico-chemical properties of the oil were determined by standard methods[2].

The gas chromatography of the oil was performed on Varian 3700 using stainless steel column (10'×1/8") packed with 100-120 mesh chromosorb-G HP coated with 5% OV-101. The essential oil was analysed by GC/MS (Finnigan model 4000 GC/MS with data system) using 25 meter fused silica capillary column coated with SE-30. The programming was done from 80 to 200° at 5°/min. Helium was the carrier gas. The ionization energy used in MS was 70 eV under EI conditions. The mass spectra in the GC/MS analysis were recorded corresponding to the GC peaks and percentage area covered by each peak was also determined.

Results and Discussion

The essential oil from the fresh plant material was obtained in 0.1% yield. The physico-chemical properties determined are, specific gravity, 0.9120/20°; ref. index, 1.4856/20°; acid value, 1.02; ester value, 3.11; ester value after acetylation, 95.24; and carbonyl value as $C_{10}H_{16}O$, 2.2. The physico-chemical data indicate that the acids, esters and the carbonyl compounds constitute about 6% of the oil. The ester value after acetylation shows high percentage of alcohols in the oil.

TABLE 1—CONSTITUENTS OF ESSENTIAL OIL OF *H. elodeoides*

Compound	Content in oil %	M^+	m/e (100%)
Hydrocarbons			
Nonane	0.83	128	43
α-Pinene	1.03	136	93
β-Pinene	0.78	136	93
Myrcene	0.56	136	93
Limonene	3.70	136	68
α-Curcumene	2.34	202	119
trans-β-Farnesene	19.21	204	69
allo-Aromadendrene	8.33	204	41
Bergamotene	4.56	204	93
γ-Muurolene	1.71	204	161
Calamenene	1.86	202	159
β-Bisabolene	7.37	204	69
Caryophyllene	3.58	204	41
Alcohols			
α-Terpeniol	0.62	154	59
Lavandulol	0.87	154	69
Elemol	5.26	222	93
Farnesol	5.16	222	69
β-Santalol	0.34	222	93
β-Bisabolol	2.10	220	81
Cedrol	21.38	222	95
Unidentified	2.77	220	60
Phenol			
7-Hydroxycalamenene	0.95	218	175

The mass spectra were identified by comparison of the spectra with those of authentic samples and published results[3-9]. One aliphatic hydrocarbon (0.83%), 4 monoterpene hydrocarbons (6.07%), 8 sesquiterpene hydrocarbons (48.96%), 2 monoterpene alcohols (1.49%), 5 sesquiterpene alcohols (34.24%)

and 7-hydroxycalamenene (0.95%) identified in the oil are given in the Table 1.

Acknowledgement

We are thankful to Mr. A. Greeley, University of California, Irvine for GC/MS of the samples.

References

1. K. R. KIRTIKAR and B. D. BASU, "Indian Medicinal Plants", Periodical Experts, Delhi, 1975, Vol. I, p. 253.
2. E. GUENTHER, "The Essential Oils", D. Van Nostrand Reinhold and Co., New York, 1949, Vol. I.
3. E. VON SYDOW and R. RYHAGE, *Acta Chem. Scand.*, 1963, **17**, 2025.
4. Y. MASADA, "Analysis of Essential Oils by Gas Chromatography and Mass Spectrometry", John Wiley, New York, 1976.
5. C. S. MATHELA, "Personal Compilation of Mono- and Sesquiterpenoids".
6. M. G. MOSHONAS and E. D. LUND, *Flavour Ind.*, 1970, **1**, 375.
7. J. ANDERSSON and E. VON SYDOW, *Acta Chem. Scand.*, 1964, **18**, 1105.
8. E. VON SYDOW, *Acta Chem. Scand.*, 1963, **17**, 2504.
9. L. H. ZALKOW, J. T. BAXTER, R. J. MCCLURE and M. M. GORDON, *J. Nat. Prod.*, 1980, **43**, 598.

J. Indian Chem. Soc.,
Vol. LXI, September 1984, pp. 794-796

Iodometric Microdetermination of Certain Carboxylic Acids by Potentiometric Titration Method

(MISS) R. SAXENA and R. M. VERMA

Department of Post-Graduate Studies and Research in Chemistry, University of Jabalpur, Jabalpur-482 001

Manuscript received 4 October 1982, accepted 10 August 1984

A potentiometric titration method is described for the microdetermination of certain carboxylic acids. The sample solution containing 0.01-0.1 meq of the acid is treated with an excess of potassium iodate and potassium iodide and the liberated iodine is titrated with thiosulphate potentiometrically using platinum-calomel electrode combination. The end-points obtained are sharper than those observed in the titration with alkali using glass-calomel electrode system. Further, the proposed iodometric titrations are applicable at a comparatively much lower concentrations of the acids tested. The results are accurate within 0 5%.

THE carboxyl function can be determined by titration against standard alkali using phenolphthalein as indicator. But in the microdetermination of weakly dissociated carboxylic acids the difficulties are : small inflection on the *p*H-neutralisation curve which progressively shortens with increasing dilution, rapid fading of the phenolphthalein colour at the end-point, and interference due to carbon dioxide[1]. In the alkalimetric procedure, the content of the titration flask are boiled for a few seconds to expel the absorbed carbon dioxide. If the acid being estimated is volatile, arrangement has to be made to prevent loss due to volatalisation[2].

For acids that give poor titration curves in aqueous solution, a non-aqueous medium can be used. The solvent selected is protophilic so that the value of the dissociation constant of the acid in question is increased. The problem with these basic solvents is that they absorb carbon dioxide readily. Thus lithium aluminium hydride or sodium triphenylmethyl cannot be used as 0.01 *N* standard solution due to their extreme sensitivity to carbon dioxide, oxygen and moisture. Further, an indicator that gives sharp end-points with 0.1 *N* titrant might be unsatisfactory for microdeterminations using 0.01 *N* standard solutions[1].

In the potentiometric titration of a weak acid with standard alkali using glass-calomel electrode combination, the formation of a buffer has an adverse effect on the sharpness of the end-point[3]. With non-aqueous solvents the potential jump near the end-point decreases with decreasing value of their dielectric constants. It has also been observed that in highly basic solvents the glass electrode does not function properly[4].

The present communication describes an iodometric procedure for the potentiometric microdetermination of some carboxylic acids. The sample solution is treated with an excess of potassium iodate and potassium iodide followed by the potentiometric titration of the liberated iodine with standard thiosulphate employing platinum-calomel electrode assembly. The reactions involved are

$$HA \rightleftharpoons H^+ + A^-$$

$$1/6\ IO_3^- + 5/6\ I^- + H^+ \rightarrow 1/2\ H_2O + 1/2\ I_2$$

$$1/2\ I_2 + S_2O_3^{2-} \rightarrow 1/2\ S_4O_6^{2-} + I^-$$

1 ml 0.001 *N* thiosulphate = 0.045 mg COOH group. The end-points obtained in the proposed procedure are quite sharp even with 0.001 *N* thiosulphate in contrast with the acid-base titration using glass-calomel electrode combination.

Experimental

Reagents : The following solutions were preared using A.R. grade chemicals and conductivity water : 0.0166 *M* (=0.1 *N*) potassium iodate ; 5% (w/v) solution of potassium iodate ; 0.1 *N* sodium thiosulphate standardised with potassium iodate[4], 0.01, 0.005, 0.0016 and 0.001 *N* solutions prepared by dilution ; 1% (w/v) fresh starch solution ; 0.1 *N* oxalic acid, suitably diluted to obtain 0.01, 0.005, 0.0016 and 0.001 *N* solutions ; 0.1 *N* sodium hydroxide prepared by titration with standard oxalic acid, and diluted to 0.01, 0.005 0.0016 and 0.001 *N* ; 1% (w/v) phenolphthalein solution in 1 : 1 ethanol-water mixture ; 0.1 *N* carboxylic acid solutions prepared by titration with standard alkali and diluted suitably to prepare test solutions.

Apparatus : A digital *p*H meter having glass-calomel electrode combination and a titration potentiometer with platinum-calomel electrodes were used for performing the potentiometric titrations.

Procedure : To a sample solution (5-10 ml) containing 0.01-0.1 meq of the acid, 1 g potassium iodide and 4 ml 5% potassium iodate solution were added and the mixture was stirred by means of a magnetic stirrer. A platinum and a calomel electrode were dipped into the solution and connected to a potentiometer. Thiosulphate solution (0.001-0.01 *N*) was

TABLE 1—MICRODETERMINATION OF SOME AROMATIC CARBOXYACIDS BY POTENTIOMETRIC TITRATION METHOD

Acid taken** mg	Iodometry			Alkalimetry		
	Found mg	Average* deviation %	Standard* deviation %	Found mg	Average* deviation %	Standard* deviation %
Benzilic						
22.824	22.842	0.08	0.13	22.842	0.08	0.20
11.412	11.421	0.08	0.20	11.469	0.50	0.55
3.804	3.810	0.16	0.26	—	—	—
2.282	2.288	0.26	0.27	—	—	—
p-Nitrobenzoic						
16.712	16.725	0.08	0.20	16.725	0.08	0.20
8.356	8.369	0.16	0.26	8.397	0.49	0.45
2.785	2.792	0.25	0.27	—	—	—
1.671	1.676	0.30	0.38	—	—	—
2,6-Dinitrobenzoic						
21.212	21.229	0.08	0.20	21.229	0.08	0.20
10.606	10.623	0.16	0.20	10.660	0.51	0.55
3.535	3.544	0.25	0.27	—	—	—
2.121	2.127	0.28	0.38	—	—	—
o-Chlorobenzoic						
15.657	15.670	0.08	0.13	15 670	0.08	0.20
7.828	7 835	0.09	0.20	7.835	0.09	0.20
2.610	2.614	0 15	0.26	—	—	—
1.565	1.569	0.26	0.27	—	—	—
Acetylsalicylic						
18.015	18.030	0.08	0.20	18.074	0.33	0.26
9.007	9.021	0.16	0.26	9.066	0.66	0.26
3.002	3.010	0.27	0.27	—	—	—
1.801	1.807	0.33	0.37	—	—	—
Phthalic						
8.300	8.306	0.07	0.13	8.368	0.80	0.26
4.150	4.153	0.07	0.20	4.201	1.22	0.27
1.383	1.385	0.14	0.26	—	—	—
0.830	0.832	0.24	0.27	—	—	—

* Calculated from six determinations.

** The 0.1 *N* solutions of acids prepared in 1 : 1 water-ethanol and diluted to obtain test solutions. Due to poor solubility of phthalic acid 0.025 *N* solution was prepared and suitably diluted.

periodically added through a microburette. After each addition, the solution was stirred and potentiometer reading recorded. The end-point was located by plotting the volume of the titrant added *vs* $\Delta E/\Delta V$, and a sharp peak in the graph indicated the end-point. ΔE is the change in potential resulting from the addition of ΔV, a definite volume of the titrant.

The thiosulphate solution was standardised potentiometrically with standard oxalic acid solution by the same procedure described above for titrating the sample solution. The concentration of oxalic acid solution, used for standardising thiosulphate, should be comparable to the acid present in the sample solution.

Results and Discussion

The proposed iodometric procedure was applied to the microdetermination of some carboxylic acids of different nature. The potentiometric titrations were performed at four concentration levels, the amounts of acids taken being 0.01-0.1 meq. The results are recorded in Table 1. The recovery studies show that the average deviation is between 0.2-0.5%, whereas the standard deviation is in the range 0.2-0.4%.

The titrimetry of a carboxylic acid with a strong base does not yield accurate results when the acid content of the sample is 0.05 meq[6] or less owing to a drawn-out indistinct end-point. In performing a potentiometric titration with glass-calomel electrodes, the potential jump at the end-point is about 30 mV/0.1 ml of 0.01 *N* sodium hydroxide as the titrant. This potential jump progressively decreases with the dilution of the titrant and the sample solution. When a sample containing about 0.025 meq acid is titrated with 0.0025 *N* alkali, the potential jump in the vicinity of the equivalence-point is very small and a series of equal jumps is observed so that the end-point cannot be located as shown in Table 1.

The proposed method involves the addition of an excess of potassium iodate and potassium iodide

to the sample solution and subsequent potentiometric titration of the liberated iodine with standard thiosulphate using platinum-calomel electrodes combination. By carrying out a large number of preliminary experiments it was concluded that by adding 4 ml 5% potassium iodate and 1 g potassium iodide to sample solutions containing 0.01-0.1 meq of acids, the quantitative liberation of iodine could be accomplished. The potentiometric titration required 15-20 min which is enough for the completion of the reaction, hence, it is not necessary to allow time before starting the titration. The potential jump at the end-point was found to be 60-100 mV/0.1 ml of 0.001-0.01 *N* thiosulphate titrant. Fig. 1 shows the potentiometric titration curves obtained by titrating 10 ml of 0.001 *N* nitrobenzoic acid with 0.001 *N* sodium hydroxide and iodometric titration with 0.001 *N* thiosulphate.

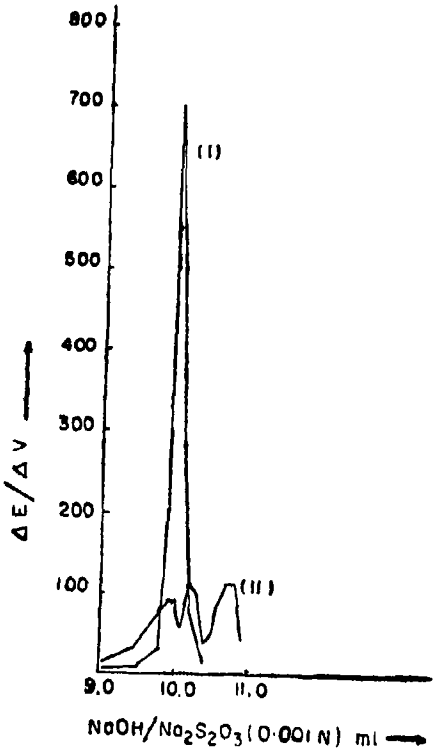


Fig. 1. Potentiometric titration of 10 ml of 0.001 *N* *p*-nitrobenzoic acid. Curve (I) obtained by the proposed iodometric method and (II) by acid-base potentiometry.

The proposed method does not require any special reagents and experimental conditions are not critical. The end-point is quite sharp even with samples containing 0.01 meq acid. Hence, the iodometric method is quite suitable for determining carboxylic acids tested, at micro level. The added advantage of the method is that it can be applied to estimate acid content in those samples which contain a component capable of reacting with alkali[6].

Acknowledgement

The authors are grateful to C.S.I.R., New Delhi for the award of a Fellowship to one of them (R.S.).

References

1. N. D. CHERONIS and T. S. MA, "Organic Functional Group Analysis by Micro and Semimicro Methods", Interscience, New York, 1964, p. 402, 485.
2. G. KAINZ, *Mikrochemie*, 1950, **35**, 89.
3. P. O. KOSONEN, *Finn. Chem. Lett.*, 1975, **5**, 121.
4. R. D. TIWARI and J. P. SHARMA, "Determination of Carboxylic Functional Groups", Pergamon Press, 1970, p. 25.
5. A. STEYERMARK, "Quantitative Organic Analysis", Academic Press, New York, 1961, p. 412.
6. N. R. KAMATH and V. B. MAINKER, *Anal. Chem.*, 1950, **22**, 724.

NOTES

Factors Influencing the Formation of Mixed Ligand Complexes of Neodymium(III)

D. N. SHELKE*

Department of Chemistry, Marathwada University, Aurangabad-431 004

Manuscript received 21 June 1982, revised 16 May 1984, accepted 10 August 1984

THERE has been a recent increase in interest of neodymium(III) chemistry due partially to an excellent review by Sigel[1] and partially to interesting properties of lanthanides which could substitute for calcium and produce an active enzyme system[2,3], particularly neodymium was better stimulator for the conversion of trypsinogen to trypsin than calcium ion[4].

The binary and ternary complexes of neodymium ion with various ligands have been extensively studied[5-9], while very little work seems to have been done in case of alkyl substituted malonic acids[10,11], and surprisingly nothing about the mixed-ligand complexes with thiodicarboxylic acids. In view of the remarkable differences in complexing abilities of the carboxylic and phenolic acids, we have reported previously the ternary complexes of neodymium(III) with substituted dicarboxylic, phenolic and pyridine carboxylic acids[12,13]. Now we report here in addition to the few data of binary complexes already reported, the equilibrium studies on the mixed ligand complex formation occuring when neodymium(III) is mixed with methyl- and dimethylmalonic acids, and thiodicarboxylic and some substituted succinic acids.

Experimental

The ligands, thiodiacetic (acetic 2,2′-thiobis, thiodiglycolic), thiodipropionic (propionic 3,3′-thiobis), methylmalonic (methylpropanedioic), dimethylmalonic (dimethylpropanedioic), succinic (butanedioic), itaconic (methylenebutanedioic) and chlorosuccinic (chlorobutanedioic) acids of Fluka (Purum) and B.D.H. (AnalaR) were used as such. Hydrated metal salt of reagent quality was obtained from B.D.H. and the concentration of metal ion was estimated gravimetrically as Nd_2O_3. Double-distilled water was used in the preparation of solutions. The details regarding other chemicals are described previously[14,15].

All pH measurements were carried out with an Elico LI-120 digital pH meter with glass and calomel electrodes having an accuracy of ± 0.01 pH unit at 30° and ionic strength 0.1 M ($NaClO_4$). The pH meter was standardised before each titration by a buffer solution of potassium hydrogen phthalate of pH value 4.01 at 30°.

Results and Discussion

Although reliable constants for the neodymium parent complexes of the methylmalonic and dimethylmalonic are not available in the literature, evaluation of formation constant necessitated the determination of these data at experimental conditions. Since stability constants of neodymium complexes of few ligands were determined earlier[12,13], the present work reports only the values obtained for the present complexes. Table 1 lists the data relating to the complexes of neodymium(III).

TABLE 1—FORMATION CONSTANTS OF NEODYMIUM(III) COMPLEXES AT 30° AND $\mu = 0.1$ M ($NaClO_4$)

Acids	K^{M}_{MX} / K^{M}_{MY} *	$K^{MY}_{MY_2}$
Methylmalonic	5.33 (2)	2.91 (1)
Dimethylmalonic	4.95 (3)	2.68 (2)
Succinic	3.38[a]	
Itaconic	3.77[a]	
Chlorosuccinic	2.42 (2)	
Thiodiacetic	3.22[b]	
Thiodipropionic	3.21[b]	

* Standard deviations in parentheses.
[a]Ref. 12, [b]Ref. 13

It is observed from the data (Table 1) that the nature of coordinating atoms for the ligands are similar and tabulated stability constants are expected by their basicities, ring size and nature of the substituent in parent acid except dimethylmalonic acid. In fact, higher stability constants should have been obtained in dimethylmalonic than methylmalonic, contrary to this, destabilised nature of these binary bis-complexes are due to steric hindrance in dimethylmalonic acid, the presence of two methyl groups substituted to the same carbon atom to which carboxylate groups are bonded. In the case of thiodiacetic and thiodipropionic, the formation constants are almost the same. If the coordination occurs through S – O, the donor sulphur atom in such complexes confers the properties which are sometimes highly novel and differ markedly from those of the analogous oxygen derivatives. In extensive studies on neodymium(III) complexes with sulphur containing ligands[16,17], the formation constants are interpreted in terms of electrostatic repulsion indicating that the contribution due to π

* Department of Chemical Engineering, Jawaharlal Nehru Engineering College, Samarth Nagar, Aurangabad-431 001.

TABLE 2—COMPLEX FORMATION CONSTANTS FOR THE MIXED LIGAND COMPLEXES OF Nd^{III}-METHYLMALONIC* AND -DIMETHYLMALONIC* WITH SUBSTITUTED SUCCINIC AND THIOACIDS** AT 30° AND $\mu = 0.1$ M ($NaClO_4$)

Acid/systems	β_{XY}	K^{a}_{DXY}	K^{MX}_{MXY}	K^{MY}_{MYX}	$\Delta \log K$
Methylmalonic-succinic	8.15 (4)	1.86	4.77	2.82	−0.56
Methylmalonic-itaconic	8.56 (2)	1.88	4.79	3.23	−0.54
Methylmalonic-chlorosuccinic	7.24 (3)	1.91	4.82	1.91	−0.51
Methylmalonic-thiodiacetic	8.02 (2)	1.89	4.80	2.69	−0.58
Methylmalonic-thiodipropionic	7.86 (3)	1.74	4.65	2.53	−0.68
Dimethylmalonic-succinic	7.78 (4)	1.72	4.40	2.45	−0.55
Dimethylmalonic-itaconic	8.11 (1)	1.66	4.34	2.78	−0.61
Dimethylmalonic-chlorosuccinic	6.80 (5)	1.70	4.38	1.47	−0.51
Dimethylmalonic-thiodiacetic	7.67 (3)	1.77	4.45	2.34	−0.50
Dimethylmalonic-thiodipropionic	7.38 (2)	1.49	4.17	2.05	−0.78

Standard deviations in parentheses.
^{a} for the reaction : $MX + MY_2 \rightleftharpoons MXY + MY$, * Ligand Y, ** Ligand X.

interaction in M−S bond is not significant. This effect is certainly reduced in neodymium complexes than uranyl[18-20].

The mixed ligand complexes were studied at a neodymium ion-ligand (X)-ligand (Y) ratio 1 : 1 : 1, under which condition formation of the species MX_2Y and MXY_2 can be neglected. The concentration of various species, H_2X, H_2Y, M, MX, MY, MY_2 and MXY and the different equilibrium constants were evaluated at TIFR Computer Centre, Bombay by the method of Ramamoorthy and Manning[21] as outlined in our earlier papers[14,15]. The corresponding data of neodymium(III) mixed ligand complexes of type MXY are given in Table 2.

The stabilisation constant, ΔlogK is the difference between measured values of stability constants which is defined by Sigel[22]

$$\Delta \log K = \log K^{MX}_{MXY} - \log K^{M}_{MY}$$

$$= \log K^{MY}_{MYX} - \log K^{M}_{MX} \qquad (1)$$

The disproportionation or mixed constant K_{DXY} can be given by reactions (2) and (3).

$$MX_2 + MY_2 \rightleftharpoons 2MXY \qquad (2)$$

$$MX + MY_2 \rightleftharpoons MXY + MY \qquad (3)$$

Table 2 suggests that ΔlogK is negative and very close to −0.6 value expected on the basis of statistical considerations, indicating thereby the preferential formation of ternary complexes than the corresponding binary. K_{DXY} values point out that the formation *via* reaction (3) of the mixed ligand complexes containing methylmalonic and dimethylmalonic is determined.

The value K_{DXY} is clearly dependent on the stabilities of the binary bis-complexes and since these bis-complexes are not intermediates in the formation of the ternary complexes, the value of K_{DXY} may not truly reflect the stability of the mixed complex. However, K_{DXY} will tend to be less dependent than ΔlogK on differences in the charges of the ligand X and Y. Hence, the choice between using ΔlogK and K_{DXY} to give a measure of stabilisation of ternary complexes will depend on the particular comparison being made. The complex stability (ΔlogK) is constant, obtained from the subtration of two equilibrium constants, and the observed values of ΔlogK are due to the lower values of binary bis-complexes, particularly in case of chlorosuccinic acid system. The slight differences present in the binary complexes are not suppressed in the ternary complexes. In addition to this, the steric hindrance in dimethylmalonic acid systems affects the stability of ternary complex and resulted into the lower values of ΔlogK, despite the two negative charges of the ligands X and Y.

It may be seen from Figs. 1 and 2 that, except thiodipropionic acid, the values of ΔlogK and K_{DXY} generally increase with decreasing the basicity of the secondary ligands. This may be explained by assuming the increased value of $\log K_1/K_2$ in parent complexes, is predominantly a consequence of steric reasons. This means that the mixed ligand complex

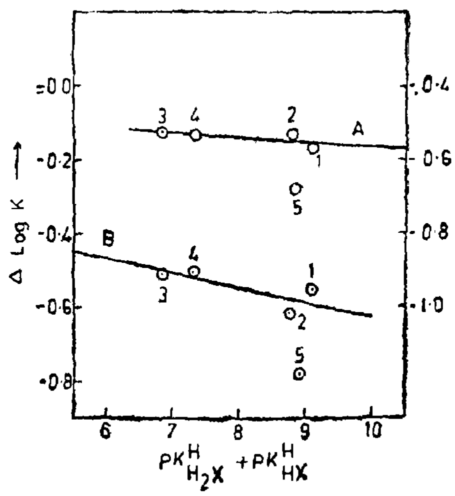


Fig. 1. Relation between ΔlogK and $pK^{H}_{H_2X} + pK^{H}_{HX}$ for mixed ligand complexes of (A) Nd^{III}-methylmalonic-dicarboxylic acids, and (B) Nd^{III}-dimethylmalonic-dicarboxylic acids. Acids : (1) succinic, (2) itaconic, (3) chlorosuccinic, (4) thiodiacetic, (5) thiodipropionic.

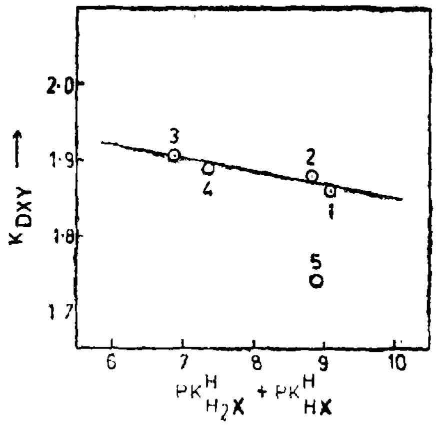


Fig. 2. Relation between K_{DXY} and $pK^H_{H_2X} + pK^H_{HX}$ for mixed ligand complexes of Nd^{III}-methylmalonic dicarboxylic acids. Acids: (1) succinic, (2) itaconic, (3) chlorosuccinic, (4) thiodiacetic, (5) thiodipropionic.

formation occurs in accordance with the stability constants of the parent complex of ligand X. Contrary to this speculation, the higher value of $\log K_1/K_2$ at least in dimethylmalonic steric hindrance may influence the mixed ligand stabilities. Because of this reason, in plots of K_{DXY} against ligand basicity relating to the mixed ligand system of dimethylmalonic acid do not gave straight line relationship between these two quantities.

It may be further established from Figs. 1 and 2 that more significant differences from the values determined for $\Delta \log K$ and K_{DXY} arise only for the various mixed ligand complexes of thiodipropionic acid (point 5). These differences, however, point to the effect resulting from the size of the chelate ring and from the specific nature of the donor atoms.

From the experimental data it is obvious that $\Delta \log K$ is most appropriate for the characterising the extra stabilisation of mixed ligand complexes[22], which has a value close to −0.6. The disproportionation or mixing constant is resulted from the differences in the stability constants of the parent complexes. On the basis of the data obtained it is further pointed out that the steric hindrance exhibited in binary bis-complexes is not significantly suppressed in ternary complexes of dimethylmalonic acid.

Acknowledgement

The financial support of U.G.C., New Delhi is gratefully acknowledged. The author is particularly indebted to Dr. Leela G. Pardeshi for useful discussions.

References

1. H. Sigel, *Met. Ions Biol. Systems*, 1973, **2**, 65, 1976, **5**, 148, 250; 1976, **6**, 273; 1979, **9**, 66, 1320.
2. D. W. Darnall and E. R. Birnbaum, *J. Biol. Chem.*, 1970, **245**, 6484.
3. D. W. Darnall and E. R. Birnbaum, *Biochemistry*, 1973, **12**, 3489.
4. D. W. Darnall and E. R. Birnbaum, *Met. Ions Biol. Systems*, 1976, **6**, 275.
5. H. S. Rana and J. P. Tandon, *Z. Phys. Chem.*, 1978, **259**, 236.
6. H. S. Rana and J. P. Tandon, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1391.
7. S D. Makhijani and S. P. Sangal, *Ann. Chem.*, 1978 **68**, 461; *J. Indian Chem. Soc.*, 1977, **54**, 670; *Chem. Era*, 1978, **14**, 387.
8. N. A. Kostromina and L. B. Novikova, *Zh. Neorg. Khim.*, 1980, **25**, 2104.
9. N. A. Kostromina, N. A. Tananaeva, L. B. Novikova and Yu B. Shevchenko, *Teor. Eksp. Khim*, 1979, **15**, 744.
10. N. A. Kostromina, T. V. Zakharov, T. V. Ternovaya and S. B. Pirkes, *Koord. Khim.*, 1978, **4**, 1526.
11. T. V. Zakharov, *Zh. Khim. Abstr.*, 1979, 7V, 57.
12. D. N. Shelke and D. V. Jahagirdar, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2142.
13. D. N. Shelke and D. V. Jahagirdar, *J. Indian Chem. Soc.*, 1979, **56**, 344.
14. D. N. Shelke and D. V. Jahagirdar, *J. Inorg. Nucl. Chem.*, 1979, **41**, 925, 929.
15. D. N. Shelke, *Inorg. Chim. Acta*, 1979, **32**, L45.
16. H. S. Rana and J. P. Tandon, *Indian J. Chem. Sect. A*, 1980, **19**, 279.
17. H. S. Rana and J. P. Tandon, *J. Indian Chem. Soc.*, 1980, **57**, 297.
18. D. N. Shelke and D. V. Jahagirdar, *J. Inorg. Nucl. Chem.*, 1981, **43**, 174.
19. D. N. Shelke and D. V. Jahagirdar, *J. Indian Chem. Soc.*, 1980, **57**, 596.
20. D. N. Shelke, *J. Indian Chem. Soc.*, 1982, **59**, 833.
21. S. Ramamoorthy and P. G. Manning, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1977.
22. H. Sigel, *Angew. Chem.*, 1975, **14**, 394.

Mass and *X*-Ray Photoelectron Spectral Studies of Bis(Acetylacetonato)-nitrosylchromium(I)

R. C. Maurya* and R. K. Shukla

Department of Chemistry, Atarra P. G. College, Atarra-210 201

and

M. R. Maurya

Regional Engineering College, Kurukshetra-132 119

Manuscript received 17 December 1982, revised 1 March 1984, accepted 10 August 1984

IN continuation of our work[1] on the synthesis and characterisation of bis(acetylacetonato)nitrosylchromium(I), studies have now been extended to mass and *X*-ray photoelectron spectroscopy of the compound.

Experimental

All chemicals were reagent grade. The mass spectrum was measured using Atlas-CH4 mass spectrometer at accelaration voltage 1500 V, and ionisation energy 70 eV. The complex is directly introduced into the ion chamber and heated to a

temperature of 210°. The photoelectronic spectrum was recorded using ESCA-3 type spectrometer using Al-K_α radiation (1846 eV) at a pressure between 5×10^{-9} and 1×10^{-8} torr. The sample was mounted on gold planchettes. The binding energy was standardised using a C(1s) binding energy of 285 eV.

The complex was prepared by the method reported earlier[1].

Results and Discussion

The nonelectrolytic complex[1] is soluble is most of the common non-polar organic solvents but insoluble in water. It is very stable and remains unaffected by concentrated alkalies or mineral acids in cold, however, decomposes on prolonged boiling. It melts sharply at 206°. The mass spectrum of [Cr(NO)(acac)$_2$] is presented in Fig. 1. Besides the parent ion peak at *m/z* 280, fragment ions like NO^+, Cr^+, Cr(acac)$^+$, CrNO(acac)$^+$, Cr(acac)$_2^+$ and Cr(acac)$_3^+$ are also observed. The most intense peak is due to Cr(acac)$^+$ observed at *m/z* 151. The origin of Cr(acac)$_3^+$ may be attributed to ion-ion interaction between Cr(acac)$_2^+$ and (acac)$^+$ ions. The molecular ion peak of low intensity, is comparable to that observed for Cr(acac)$_3^+$ and the results reported by some workers[3,4]. Thus, it is evident that the compound is monomeric in the vapour state and this result confirms to the earlier report[1].

The *X*-ray spectrum of [Cr(NO)(acac)$_2$] in the binding energy range 395-415 eV is presented in Fig. 2. The N(1s) value of 401.8 eV is comparable to that reported for the potassiumpentacyanonitrosylchromate(I)[5]. The slight increase in the value may be due to the neutral nature of the complex. The higher value also agrees well with the increase of ν_{NO} in its ir spectrum[1] compared to that of the ν_{NO} in K_3[CrNO(CN)$_5$][6]. It appears, therefore, that NO in the present compound is present as NO^+ which correlates well with the N(1s) value of the compound and agrees with that of the parent compound[3], where coordination of nitric oxide as NO^+ is already established.

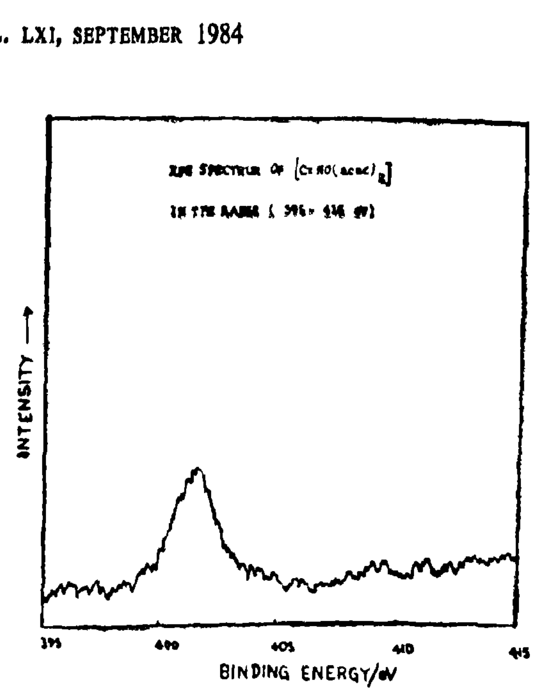


Fig. 2

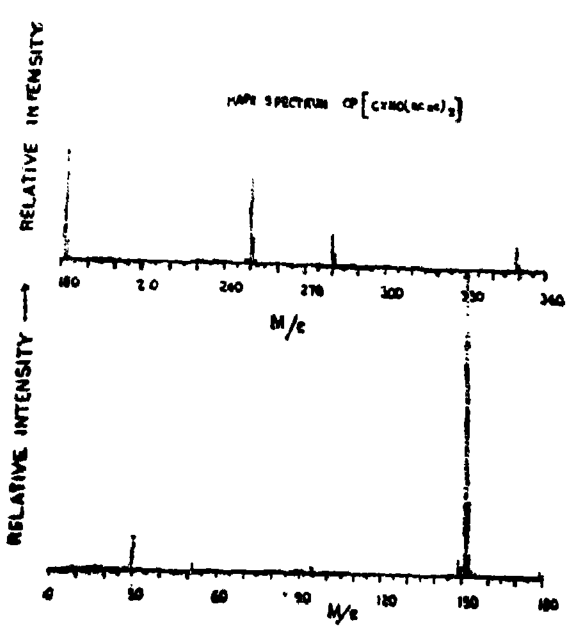


Fig. 1

Acknowledgement

The authors (R.C.M. and R.K.S.) are indebted to Dr. V. L. Gour, Principal and Sri Jagpat Singh, President of the College for facilities and encouragement. Thanks are also due to Dr. S. Sarkar, Assistant Professor, Chemistry Department, I.I.T., Kanpur for the spectra of the compound.

References

1. S. SARKAR, R. C. MAURYA and S. C. CHAURASIA, *Indian J. Chem., Sect. A*, 1976, **14**, 285.
2. C. G. MACDONALD and J. S. SHANNON, *Aust. J. Chem.*, 1966, **19**, 1545.
3. G. M. BANCROFT, C. REICHERT and J. B. WESTMORE, *Inorg. Chem.*, 1968, 7, 870.
4. M. K. CHAUDHURI, N. ROY and D. T. KHATTING, *Synth. React. Inorg. Metal-Org. Chem.*, 1983, 12, 715.
5. V. I. NEFDOV, *Naturwissenschaften*, 1976, **25** 888.
6. W. P. GRIFFITH, *J. Chem. Soc.*, 1963, 3286.

Electron Spin Resonance Study of Pseudotetrahedral Copper(II) and Tetrahedral Cobalt(II) Complexes

K. LAXMA REDDY, S. SRIHARI and P. LINGAIAH*

Department of Chemistry, University College, Kakatiya University, Warangal-506 009

Manuscript received 26 September 1983, revised 18 April 1984, accepted 18 April 1984

THE electronic spectra of Cu^{II} complexes[1] show two peaks at 13100 and 25000 cm^{-1} instead of only one peak below 10000 cm^{-1} ($^2T_2 \rightarrow ^2E$) which is characteristic of tetrahedral geometry. This was explained by the splitting of ground term $^2T_2$ into its low symmetry components in pseudotetrahedral configuration. The literature survey on esr studies of Cu^{II} complexes reveals a number of examples of complexes having distorted octahedral and square-planar geometries[2,3] and only a few of them having pseudotetrahedral geometry[4,5]. The electronic spectra of Co^{II} complexes[1] show one peak around 16000 cm^{-1} which may be assigned to $^4A_2(F) \rightarrow ^4T_1(P)$ transition, characteristic of tetrahedral configuration. The esr study of Co^{II} octahedral and tetrahedral complexes is very scarce in the literature. Recently the unusual electronic and esr spectra of pseudotetrahedral complexes of Co^{II} with different amines have been reported[6].

Therefore, it is of interest to study the esr spectra of pseudotetrahedral Cu^{II} and tetrahedral Co^{II} complexes. In continuation of our earlier work[1], we report in this note the esr study of Cu^{II} and Co^{II} complexes with 2-methyl-3-aminoquinazoline-4-one (MAQ) and 2-phenyl-3-aminoquinazoline-4-one (PAQ).

Experimental

The ligands were prepared as reported earlier[7]. The purity of the compounds was checked by tlc and melting point determination. The Cu^{II} and Co^{II} complexes were prepared using metal sulphate and metal acetate, respectively. In the preparation of all the complexes the following general procedure was adopted. Metal salt was dissolved in methanol. Methanolic ligand solution in slight excess over the 1 : 2 (metal : ligand) ratio was added to it dropwise with constant stirring. The complex was formed immediately after refluxing the reaction mixture for 30 min on water bath. It was filtered, washed several times with hot water and then with methanol until free from the reagent. The complex was dried in vacuum over anhydrous calcium chloride. The analytical data (C, H and N) for the ligands and their complexes were obtained from Micro-analytical Laboratory, University of Calcutta. The metal content in the complexes was determined using the standard procedures. The esr spectra of the solid complexes were recorded at room temperature using Varian E-4 X-band spectrophotometer. Typical spectra of Cu^{II} and Co^{II} complexes are given in Figs. 1 and 2. Spin Hamiltonian parameters like $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ have been calculated from the spectra applying the method of Kneubuhl[8]. These along with the other parameters evaluated are listed in Table 1.

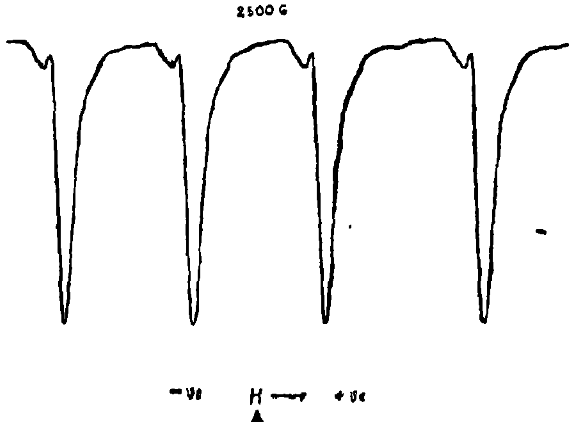


Fig. 1. Esr spectrum of Cu^{II}—MPQ.

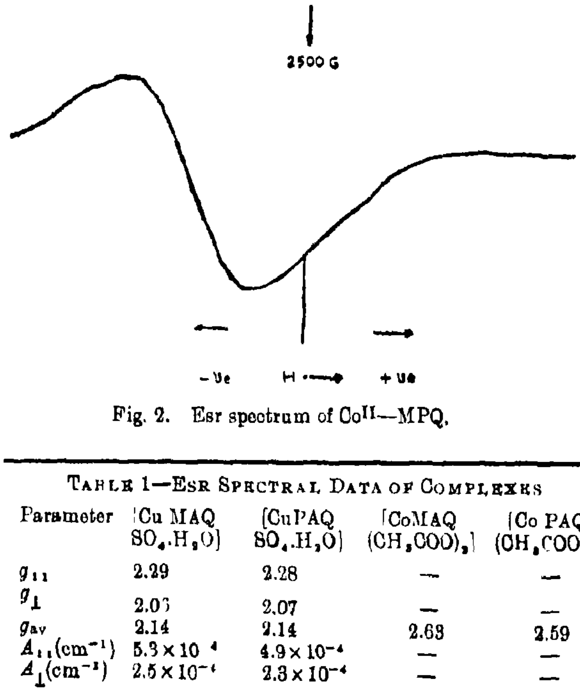


Fig. 2. Esr spectrum of Co^{II}—MPQ.

TABLE 1—ESR SPECTRAL DATA OF COMPLEXES

Parameter	[Cu MAQ $SO_4.H_2O$]	[CuPAQ $SO_4.H_2O$]	[CoMAQ $(CH_3COO)_2$]	[Co PAQ $(CH_3COO)_2$]
$g_\parallel$	2.29	2.28	—	—
$g_\perp$	2.03	2.07	—	—
g_{av}	2.14	2.14	2.63	2.59
$A_\parallel(cm^{-1})$	5.3×10^{-4}	4.9×10^{-4}	—	—
$A_\perp(cm^{-1})$	2.5×10^{-4}	2.3×10^{-4}	—	—
$A_{av}(cm^{-1})$	3.43×10^{-4}	3.17×10^{-4}	—	—
G	4.99	4.10	—	—
$K^2_\parallel$	0.57	0.55	—	—
$K^2_\perp$	0.30	0.35	—	—
$-\lambda_0(cm^{-1})$	828	828	—	—
$-\lambda(cm^{-1})$	471	454	—	—

Results and Discussion

The elemental analyses (C, H, N and metal) of the complexes indicate that their composition can

be represented as [$CuLSO_4.H_2O$] and [CoL $(CH_3COO)_2$], where L=MAQ or PAQ.

Cu^{II} ion having d^9 configuration can form complexes of octahedral, square-planar and tetrahedral geometries. Because of the Jahn-Teller effect the distortion occurs from the regular geometries in Cu^{II} complexes. The distortion depends on the presence of unpaired electron in different orbitals. In an elongated octahedron the unpaired electron lies in $d_{x^2-y^2}$ orbital whereas in compressed octahedron it lies in d_{z^2} orbital. In a pseudotetrahedral Cu^{II} complexes the unpaired electron lies in d_{xy} orbital. On the basis of g tensor values, Singh concluded that $g_{\parallel} > g_{\perp}$ in an elongated octahedron, whereas $g_{\parallel} < g_{\perp}$ in compressed form[9]. Sharnoff observed that $g_{\perp} < g_{\parallel}$ in pseudotetrahedral Cu^{II} complexes[10].

The esr spectra of Cu^{II} complexes of MAQ and PAQ exhibit a set of four hyperfine lines, which result from the coupling of ^{63}Cu nucleus ($I=3/2$) with the unpaired electron. Cu^{II} complexes with tetrahedral geometry, where the ground term is essentially $^2T_2$, show two characteristic properties: (i) their esr signals are observed only at very low temperature and (ii) the g values are very widely different from 2.0023. This is because the three states of T_2, close in energy, are connected by the spin orbital operator. The present Cu^{II} complexes, on the other hand, show esr signals at room temperature and also the g values are not far from 2.0023 (Table 1). This suggests that the ground term is not essentially $^2T_2$ and that some of its orbital degeneracy is lifted by the low symmetry component of the ligand field. This supports the observation made earlier from the electronic spectra of these complexes[1]. From Table 1, it can be seen that the $g_{\parallel}$ obtained for the complexes is less than 2.3 indicating covalent character of the metal-ligand bond[9]. The axial symmetry parameter G, defined as $g_{\parallel}-2.0023/g_{\perp}-2.0023$, is found to be greater than 4, suggesting that there is no interaction between copper centres in the solid state[11]. Further, orbital reduction parameters have been calculated[12] and the values of $K_{\parallel}^2$ are greater than those of $K_{\perp}^2$, indicating that the complexes are of out-of-plane-π-bonded type. Spin orbit coupling constant (λ) for the complexes is less than that of the free metal ion (λ_0) suggesting mixing of ground and excited terms.

The esr study of octahedral and tetrahedral Co^{II} complexes is of large interest. The ^4F state of Co^{II} in an octahedral field is split into three states with $^4T_{2g}$ state lowest in energy. Since these states are connected by the spin orbit coupling, the spin-lattice relaxation times are short, making esr measurements possible only at low temperatures. But in tetrahedral field, ^4F state of the d^7 system has the orbital singlet state ($^4A_2$), lowest in energy and with all excited states being at much higher energies. This situation gives rise to relatively large spin lattice relaxation times and gives narrow esr absorption lines even at room temperature[12]. But in contrast, the resolution of esr spectra of the present Co^{II} complexes at room temperature is poor due to which different g and A values could not be obtained. However, from the single broad band observed, g_{av} has been calculated (Table 1).

Acknowledgement

The authors wish to thank Prof. A. K. Bhatnagar, University of Hyderabad for providing esr spectra. One of the authors (K.L.R.) is thankful to the C.S.I.R., New Delhi for the award of a Senior Research Fellowship.

References

1. K. L. Reddy, S. Srihari and P. Lingaiah, *J. Indian Chem. Soc.*, 1983, **60**, 1020.
2. D. Kivelson and R. Neiman, *J. Chem. Phys.*, 1961, **35**, 149.
3. A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 1958, **29**, 35.
4. M. Sharnoff, *J. Chem. Phys.*, 1965, **42**, 3383.
5. C. R. Rosenberg, A. C. Root, K. P. Bernstein and B. H. Gray, *J. Am. Chem. Soc.*, 1975, **97**, 2092.
6. L. Banci, O. Bencini, D. Gatteschi and F. Mani, *Inorg. Chem.*, 1982, **21**, 1133.
7. L. Legrand and N. Lozach, *Bull. Soc. Chim. Fr.*, 1961, 1400 (*Chem. Abstr.*, 1962, **56**, 11591).
8. F. K. Kneubuhl, *J. Chem. Phys.*, 1960, **33**, 1074.
9. S. Chandra, K. B. Pandeya and R. P. Singh, *Indian J. Chem., Sect. A*, 1979, **18**, 476.
10. M. Sharnoff, *J. Chem. Phys*, 1965, **42**, 3383.
11. B. J. Hathaway, *Struct. Bonding (Berlin)*, 1973, **14**, 60.
12. L. Richard Carlin, "Transition Metal Chemistry", Marcel-Dekker, New York, 1966, Vol. 3, pp. 182, 163.

Studies on Copper(II) Mixed β-Diketonates and Their Adducts with Nitrogen Bases

R. C. MISHRA, P. K. MISHRA, B. K. MOHAPATRA*

Department of Chemistry, B. J. B. College, Bhubaneswar-751 014

and

D. PANDA

V. Deb College, Jeypore

Manuscript received 11 April 1983, revised 9 March 1984, accepted 10 August 1984

THE chemistry of metal β-diketonates has aroused much recent interest in such diverse areas[1] as spectral studies, gas chromatography, solvent extractions, column and thin layer chromatography, nmr shift reagents, laser technology and as initiators in free radical polymerisation[2]. The quasi-aromatic character of such compounds have also received considerable attention. The formation of adducts of metal β-diketone chelates plays an important role in the synergistic enhancement of the solvent extraction of metal ions[3]. Several base adducts of zinc(II) and copper(II) β-diketonates were previously reported by us[4-8]. As a part of the general programme on studies on the linkage modes of β-diketones in transition metal complexes the lability of the

β-diketonate moiety was investigated. Lability studies on the central carbon bonded palladium(II) and platinum(II) β-diketonates have been reported earlier[9,10]. This communication describes the reaction between $Cu(acac)_2$ ($acac^-$ = acetylacetonate) and other copper(II) β-diketonates to form mixed chelates, which subsequently react with quinoline to produce mono- or bis-adducts.

Experimental

All the chemicals used were of reagent grade (B.D.H., E. Merck or Fluka). Copper(II) β-diketonates were prepared[4] by reacting an aqueous solution of copper(II) acetate and an ethanolic solution of the respective β-diketones taken in 1 : 2 molar proportion. The solutions were stirred magnetically for 30 min over gradual addition of β-diketone solutions. The precipitated compounds were filtered under suction, washed with ethanol and ether, and dried in a vacuum desiccator.

$Cu(acac)_2$ and other copper(II) β-diketonates in the molar ratio 1 : 1 were dissolved in 20 ml of benzene and the solution refluxed for 30 min. Volume of the resulting solutions were concentrated to 5 ml in a rotary vacuum evaporator and the concentrated solution was kept overnight in a refrigerator when crystalline compounds separated out. These mixed chelates were filtered under suction, washed with a small amount of benzene and ether, and dried in a vacuum desiccator.

The mixed chelates were dissolved in 10 ml of benzene and treated with quinoline (molar ratio 1 : 2) and stirred magnetically at 40°C for 30 min. Solutions were concentrated to 5 ml, and kept in a refrigerator overnight. The crystalline compound obtained was filtered out, washed with ether and ultimately dried in a vacuum desiccator over liquid paraffin. Analysis and physical measurements were made as reported earlier[11]. Relevant analytical data are presented in Table 1 and spectral data in Table 2.

Results and Discussion

The mixed chelates are blue or green in colour and have the composition Cu(acac)(L), where L is the anion of tfac, hfac, dpm, tta or pta. The base adducts are either green or blue crystalline solids and are monoadducts having the composition Cu(acac)(L)Q except the green compound Cu(acac)(hfac)(Q_2) which is a bis-adduct. These are soluble in common organic solvents. They have fairly low melting points, and 0.001 *M* acetone solutions of the complexes have very low molar conductance values (Table 1) indicating non-electrolytic nature. Magnetic moment values indicate the presence of one unpaired electron expected for a copper(II) ion. The base adducts are fairly stable in air unlike the adducts of bis-(acetylacetonate)copper(II), as evidenced by the fact that they do not lose the base on exposure to air for several days. Important infrared spectral bands have been assigned on the basis of earlier studies by Nakamoto[12]. $\nu_{C=O}$ bands of the mixed chelates are given in Table 2.

TABLE 1—ANALYTICAL DATA

Sl. no.	Compd.*	M.p. °C	Λ_M $\Omega^{-1}cm^2$	μ_{eff} B.M.	Analysis % : Found/(Calcd.) metal	N
1.	Cu(acac)(tfac)	125	9	1.79	20.45 (20.13)	—
2.	Cu(acac)(hfac)	108	6	1.79	17.54 (17.19)	—
3.	Cu(acac)(dpm)	105	11	1.83	17.98 (18.38)	—
4.	Cu(acac)(pta)	118	7	1.82	17.46 (17.76)	—
5.	Cu(acac)(tta)	128	11	1.82	17.22 (17.00)	—
6.	Cu(acac)(tfac)Q	110	8	1.82	14.01 (14.32)	3.36 (3.15)
7.	Cu(acac)(hfac)Q_2	98	7	1.80	10.43 (10.15)	4.22 (4.47)
8.	Cu(acac)(dpm)Q	95	11	1.81	13.12 (13.41)	2.72 (2.95)
9.	Cu(acac)(pta)Q	107	10	1.81	12.85 (13.09)	2.64 (2.88)
10.	Cu(acac)(tta)Q	105	7	1.83	13.28 (12.66)	2.96 (2.79)

* Anions : acac = acetyl acetone, dpm = dipivaloyl methane, tta = thenoyltrifluoroacetone, tfac = trifluoroacetylacetone, hfac = hexafluoroacetylacetone, pta = pivaloyl trifluoroacetone.

TABLE 2—INFRARED (cm^{-1}) AND ELECTRONIC SPECTRAL DATA

Sl. no.	$\nu_{C=O}+\nu_{C=C}$	ν_{M-O}	ν_{M-N}	ν_{max} in kK (ε)
1.	1610, 1600, 1580, 1560	450, 400	—	580 (30), 680 (35)
2.	1645, 1615, 1600, 1560	450, 420	—	650 (25)
3.	1590, 1560, 1580, 1475	460	—	580 (30), 650 (35)
4.	1600, 1560, 1580	450, 410	—	580 (25), 675 (35)
5.	1605, 1600, 1580, 1560	400, 420	—	560 (25), 680 (30)
6.	1625, 1610, 1580	430	300	700 (70)
7.	1615, 1610, 1560	435	305	690 (68)
8.	1600, 1570, 1550	450	310	680 (65)
9.	1615, 1610, 1580	430	300	690 (60)
10.	1620, 1605, 1590	435	295	700 (65)

In the mixed chelates there are two distinct set of $\nu_{C=O}$ bands assignable to the two different β-diketonate moieties. In the cases of base adducts it is observed that the $\nu_{C=O}$ bands have shifted to a higher frequency region while the ν_{M-O} bands to a lower frequency region on coordination with the nitrogen bases. Further, most of the absorption bands due to free nitrogen ligands are shifted in the base adducts. Bonding of the nitrogen ligands has been substantiated by the observation[13] of ν_{Cu-N} bands at ~290-310 cm^{-1} region in the far-infrared spectra.

Visible electronic spectra of the mixed chelates and their base adducts in chloroform and chloroform-base solutions have been studied and the absorptions bands are recorded in Table 2. The mixed chelates usually give rise to two absorption

bands with their extinction coefficients being 25 and 35. In the case of base adducts only one absorption band is observed around 680-700 nm region very near to the second band of the mixed chelates. Eventhough, the position of this band has not changed much in the base adducts, the intensity of the band is relatively higher. A clear isobestic point and high extinction coefficient value indicate that only two species are involved. With increased amounts of base being added, the intensity goes up but the position of band maxima does not change appreciably. In the case of bis-adduct (compd. 6) the intensity value is quite high. It was observed[14-17] that in the case of base adducts, the extinction coefficient values increase without much shifting of the band maxima. Our observations are similar to those mentioned above. Therefore, it appears that all the adducts are presumably penta-coordinated mono-adducts of the mixed chelates except the adduct of (hfac) which is a six-coordinated bis-adduct. Formation of the mixed chelates reveals the lability of the β-diketonate moiety.

The enhanced stability of the base adducts of mixed chelates is due to the increasing Lewis acid character of the chelates as a result of the replacement of one of the acetylacetonato group by a β-diketonate having electron withdrawing substituents.

References

1. K. C. JOSHI and V. N. PATHAK, *Coord. Chem. Rev.*, 1977, **22**, 37.
2. G. H. BAMFORD and D. J. LIND, *Proc. R. Soc. Ser. A*, 1967, 146 ; 1969, 302.
*3. W. R. WALKER and N. C LI, *J. Inorg. Nucl. Chem*, 1965, **27**, 411.
4. B. K. MOHAPATRA and V. D. RAMAN RAO, *Z. Anorg. Allg. Chem.*, 1970, **732**, 332.
5. B. K. MOHAPATRA and D. V. RAMAN RAO, *Inorg. Chim. Acta*, 1970, **4**, 404.
6. B. K. MOHAPATRA, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3930.
7. B. K. MOHAPATRA, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3929.
8. B. K. MOHAPATRA, *J. Prakt. Chem.*, 1973, **315**, 347.
9. B. K. SAHU and B. K. MOHAPATRA, *Indian J. Chem., Sect. A*, 1982, **21**, 730.
10. B. K. SAHU and B. K. MOHAPATRA, *Polyhedron*, in the press.
11. A. SAMANTARAY, P. K. PANDA and B. K. MOHAPATRA, *J. Indian Chem. Soc.*, 1981, **58**, 408.
12. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compound", John Wiley, New York, 1963, p. 224.
13. J. R. FERRARO, "Low Frequency Vibrations of Inorganic and Coordination Compounds", Plenum Press, New York, 1971.
14. D. P. GRADDON and E. C. WATTON, *J. Inorg. Nucl. Chem.*, 1961, **21**, 49.
15. W. R. WALKER and N. C. LI, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2255.
16. T. SHIOMATSU, M. TABUSHI, M. MATSUI and M. MUNNATA, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2656.
17. P. E. RAKITA, S. J. KOPPERL and J. P. FACKLER, JR., *J. Inorg. Nucl. Chem.*, 1968, **30**, 2139.

Reactions of 2,4-Pentanedionato Complexes
Bromination of Tris(2,4-pentanedionato) iron(III)

N. H. PAIKE

Department of Chemistry,
Shri Sharanabasaveshwar College of Science,
Karnataka-585 103

Manuscript received 5 November 1982, revised 16 August 1983, accepted 10 August 1984

An extensive work has been reported[1-5] on the physico-chemical properties of tris(2,4-pentanedionato)iron(III), $Fe(acac)_3$. The bromination reactions of $Cu(acac)_2$ and $Co(acac)_3$ suggested[6,7] that the reaction conditions have a deciding effect on the nature of the reaction products. This view was also supported from the reaction of powdered solid $Ni(acac)_2$, with liquid bromine[8]. The reaction resulted in the oxidative decomposition of the complex, producing $Ni^{III}Br_3$ which was confirmed by a number of observations. This gave the initiation to carry out the bromination reaction of $Fe(acac)_3$ in a similar manner. Some interesting observations and findings on the reaction of $Fe(acac)_3$ with liquid bromine and reactions of brominated product with various ligands have been elucidated in this paper.

Experimental

Tris(2,4-pentanedionato)iron(III) was synthesised and purified by the reported method[9]. Finely powdered tris(2,4-pentanedionato)iron(III) (0.3 mol) was treated with liquid bromine (3 mol). The reaction was allowed to complete at room temperature in dry atmosphere. After the completion of the reaction, unreacted bromine was removed by repeated washings with n-heptane. The removal of unreacted bromine was tested with aqueous potassium iodide solution (10%). The brominated product was dark red at room temperature, vacuum dried and solidified in dry-ice.

The elemental analyses of C and H were done at Micro Analytical Division of the Chemistry Department, University of Poona. Measurements of the electrical conductivity were carried out on Philips GM 4144 conductivity bridge. The half-wave potentials ($E_{\frac{1}{2}}$) of the reaction product were made on the polarographic instrument at the Central Electro Chemical Research Institute, Karaikudi. Electronic spectra were recorded in solution on Backman DB spectrophotometer. Magnetic susceptibilities of the brominated product were measured from 100 K to room temperature on Gouy type balance at the Indian Institute of Technology, Bombay. The epr spectra were recorded on standard Varian E-4 instrument and at Indian Institute of Technology, Madras.

Results and Discussion

A dark red viscous mass was obtained when finely powdered $Fe(acac)_3$ was allowed to react with liquid bromine. The product of the reaction was a

TABLE 1—ELEMENTAL ANALYSIS OF BROMINATED PRODUCT

Compound	Molecular formula	Analysis % ; Found/(Calcd.) Fe	C	H	Br	Colour	Solubility
$Fe(acac)_3$	$C_{15}H_{21}O_6Fe$	15.63	50.80	6.32	—	Orange	Common organic solvents
$Fe(HacacBr)Br(Br_3)_2$	$C_5H_7O_2Br_9Fe$	6.78 (6.8·)	10.21 (10.26)	— (0.85)	68.15 (68.39)	Dark red	Acetonitrile, nitrobenzene, acetone

semisolid and could be solidified in dry-ice (−70°). The red reaction product was investigated in acetonitrile solvent by the polarographic technique using lithium perchlorate as a supporting electrolyte. The result showed two irreversible waves.

$$Fe^{III} \rightarrow Fe^{II}\ (E_{\frac{1}{2}} = -0.25\ V\ vs\ SCE)\ \text{and}$$

$$Fe^{II} \rightarrow Fe^{0}\ (E_{\frac{1}{2}} = -0.98\ V\ vs\ SCE).$$

These values are in excellent agreement with the reported ones[10]. Tris(2,4-pentanedionato)iron(III), its brominated product and derivatives were subjected to elemental analysis (Table 1). On the basis of analysis the formula of the product was assigned to be $Fe(HacacBr)Br_7$. The bromine analysis by the iodometric and silver nitrate method is suggestive of the presence of two tribromide ionic species of the product. The product exhibits solution conductivity tending towards 1 : 2 electrolyte behaviour in both the solvents at room temperature[11] (Table 2).

The equilibrium constant for the ionization in acetonitrile was calculated[12] to be 4.5×10^{-3} on the basis of 1 : 1 electrolytic nature. The conductivity

TABLE 2—SOLUTION CONDUCTIVITY DATA

Solvent	0.01 M	0.005 M	0.0025 M	Λ_∞
	Λ Ω^{-1} l^{-1} M^{-1}			Ω^{-1}
Acetone	116.9	124.6	131.9	151.8
Acetonitrile	131.8	141.5	154.6	186 2

measurements showed that the reaction product is nearing 1 : 2 electrolytic nature. If the same assumption is extended towards the extraction method of calculating the equilibrium constant, then the equilibrium process would be formulated as

$$Fe(HacacBr)Br(Br_3)_2 \rightarrow Fe(HacacBr)Br_5 + 2Br$$

The equilibrium constant (Table 3) has been calculated on this formulation. It appears appropriate to call this equilibrium constant k_1 than the overall equilibrium constant as the reaction was assumed to be the decomposition of only one tribromide ion. From the reaction product it appears that to be similar to one of the few complexes of transition metals containing trihalide ion[13].

TABLE 3—DATA ON EQUILIBRIUM CONSTANT

Temp. °C	pK conductometry	pK extraction	pK, for (teab + Br), voltammetry*
25	2.35	6.87	7.3

* I.V. Nelson and T.R. Iwamoto, *J. Electroanal. Chem.*, 1968, 7, 218.

The interesting features of the product are, (i) the presence of neutral 3-bromo-2,4-pentanedione in the complex, and (ii) the presence of two Br_3^- and one Br^- as coordinating ions.

The electronic spectrum (Fig. 1) of the reaction product support the presence of the tribromide ion, and HacacBr in it. The electronic spectral assignments (Table 4) and the positions of the reaction product conform to an octahedral high spin iron(III) ion, similar to those reported in the literature for high spin iron(III) compounds. The high spin nature of the product is evidenced from the magnetic susceptibility measurements.

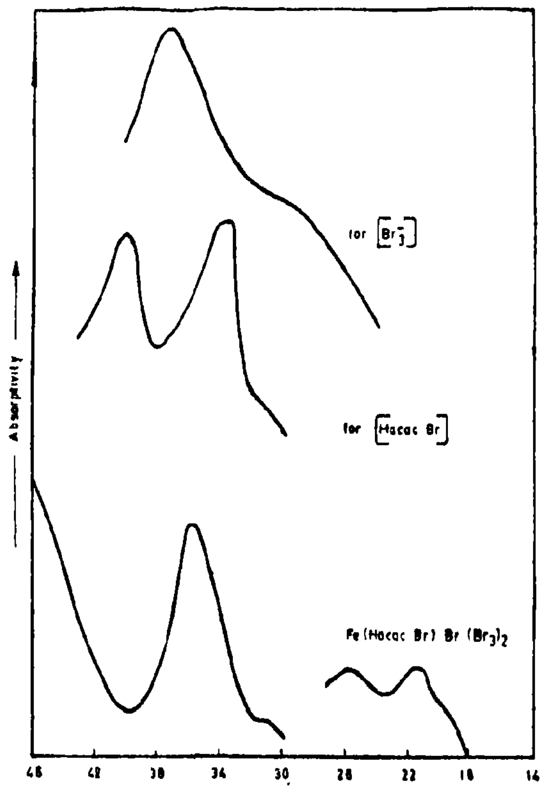


Fig. 1

TABLE 4—ELECTRONIC SPECTRA OF $Fe(HacacBr)Br(Br_3)_2$ (cm^{-1})

Solvent	ν_1 $^4T_{1g} \leftarrow {}^6A_{1g}$	$\nu_{2'}$ $^4T_{2g} \leftarrow {}^6A_{1g}$	$\nu_{3'}$ $^4A_{1g}{}^4E_g \leftarrow {}^6A_{1g}$
Acetonitrile	21645	23996	25907
Acetone	21645	23996	25907
Nitrobenzene	21505	23256	23696

The transitions due to tribromide ion were observed at 25840 and 35971 cm^{-1} and those due to the HacacBr at 31446 and 45454 cm^{-1}.

Magnetic behaviour (Table 5) of iron(III) (high spin) is quite similar to that of manganese(II). The complex shows constant magnetic moment of 5.9 ± 0.1 B.M. in the temperature range 100-300 K. Which corresponds to five unpaired electrons of the high spin iron(III).

TABLE 5—MAGNETIC SUSCEPTIBILITY DATA OF $Fe(HacacBr)Br(Br_3)_2$

Temp. K	$\chi M \times 10^6$ mol observed	$\chi M \times 10^6$ mol observed	μ_{eff} observed B.M.
100	42170	44936	5.80
160	28300	29957	5.80
165	27200	27234	5.99
176	24800	25532	5.90
188	24200	23902	6.03
200	22150	22468	5.95
240	18500	18723	5.94
260	17000	17283	5.94
280	16230	16048	6.02
300	14665	14979	5.93

Acknowledgement

The author is indebted to (late) Prof. A.B. Biswas, Indian Institute of Technology, Bombay, for his help and guidance. The author is grateful for the financial help from the U.G.C., New Delhi, and to the Principal, Shri Sharanabasaveshwar College of Science, Gulbarga for the grant of study leave.

References

1. J. P. FACKLER, JR., *Prog. Inorg. Chem.*, 1966, **7**, 361.
2. D. P. GRADDON, *Coord. Chem. Rev.*, 1969, **4**, 1.
3. D. W. THOMPSON, *Struct. Bonding (Berlin)*, 1971, **9**, 27.
4. J. HAIGH, J. K. MICHAEL and W. DAVID, *J. Chem. Soc., Faraday Trans.* 2, 1977, **73**, 1561.
5. R. G. CHARLES and S. BARNARTT, *J. Phys. Chem.*, 1958, **62**, 315.
6. Y. NAKAMURA and S. KAWAGUCHI, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 954.
7. T. OGURA, Y. KOJIMA, Y. KAKAMURA and S. KAWAGUCHI, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 1468.
8. S. B. KULKARNI, G. N. NATU, S. S. KENI and S. P. GHODKE, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1238.
9. T. MOELLER, *Inorg. Synth.*, 1957, **5**, 105, 113, 130, 188; W. C. FERNELIUS, *Inorg. Synth.*, 1954, **2**, 17, 25, 119; E. G. ROCHOW, *Inorg. Synth.*, 1958, **6**, 154.
10. J. B. HEADRIGE, "Electrochemical Techniques for Inorganic Chemists", Academic Press, New York, 1969.
11. W. J. GEARY, *Coord. Chem. Rev.*, 1971, **7**, 81.
12. J. M. WILSON, R. J. NEWCOMBE, A. R. DENARO and R. M. W. RICKETT, "Experiments in Physical Chemistry", Pergamon, Oxford, 1962, p. 104.
13. A. I. POPOV, "Halogen Chemistry", ed. V. GUTTMANN, Academic Press, New York, 1967, Vol. 1.

Formation Constant and Thermodynamic Functions of Some Trivalent Rare Earth Metal Complexes of *p*-Sulphonosalicylidenesulphanilamide

G. P. SENGUPTA and C. R. BERA

Department of Chemistry, Visva-Bharati University, Santiniketan-731 235

Manuscript received 14 December 1982, revised 25 August 1983, accepted 10 August 1984

LITERATURE survey reveals that no potentiometric studies have been done for the complex formation of trivalent rare earth metal ions with *p*-sulphonosalicylidenesulphanilamide (*p*-SUSASUD). In continuation to our earlier studies[1,2] on Schiff base ligands and their metal complexes, we report in this paper the formation constants and thermodynamic parameters of trivalent rare earth metal ion complexes of Pr^{III}, Nd^{III}, Sm^{III} and Gd^{III} with *p*-sulphonosalicylidenesulphanilamide in aqueous medium at different temperatures and ionic strengths.

Experimental

All the chemicals and reagents used were either of AR grade or purified before use.

Preparation of the ligand: The ligand, *p*-sulphonosalicylidenesulphanilamide was prepared according to literature[3]. The purity of the compound was checked by its elemental analysis and melting point determination.

Solution: Double distilled water and carbonate free sodium hydroxide[4] were prepared. Perchloric acid and sodium perchlorate solutions were prepared in double-distilled water. The metal oxides were converted to metal perchlorates and then dissolved in 0.1 *M* perchloric acid solution. Estimation of the metal ions was done by EDTA method[5].

Apparatus: A digital *p*H-meter of the Electronics Corporation of India, model 5651 (accuracy ± 0.01 units) with a combined glass electrode assembly was used. All the computations were carried out on an Electronics Corporation of India model EC 62 P progammable calculator.

Bjerrum-Calvin titration: The method of Bjerrum-Calvin[6,7] as modified by Irving and Rossotti[8] was followed to determine the proton-ligand and metal-ligand stability constants. Following sets of titrations were performed at three different temperatures 32° ($\mu = 0.1$ *M* $NaClO_4$), 42° ($\mu = 0.1$ *M*, 0.05 *M* and 0.01 *M* $NaClO_4$), and 52° ($\mu = 0.1$ *M* $NaClO_4$).

Acid titration : 10 ml 0.1 *M* $HClO_4 + NaClO_4$ solution + water.

Ligand titration : 10 ml 0.1 *M* $HClO_4 + 4 \times 10^{-3}$ *M* ligand + $NaClO_4$ solution + water.

TABLE 1—PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS OF p-SULPHONOSALICYLIDENESULPHANILAMIDE (p-SUSASUD) AND ITS COMPLEXES WITH RARE EARTH METAL IONS IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

Temp. °C	Ionic strength M $NaClO_4$	H⁺			σ*	Pr		Nd		Sm		Gd	
		$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta_n^H$	$\log K_1$	σ	$\log K_1$	σ	$\log K_1$	σ	$\log K_1$	σ
32	0.1	10.14	6.76	2.30	0.03	7.04	0.16	7.70	0.18	8.43	0.17	8.27	0.14
42	0.1	10.25	6.86	2.00	0.03	6.91	0.17	7.50	0.18	8.14	0.14	7.92	0.13
42	0.05	10.25	6.98	2.18	0.01	7.25	0.17	7.88	0.16	8.65	0.18	8.22	0.18
42	0.01	10.27	7.15	2.23	0.01	7.76	0.16	8.33	0.17	9.28	0.16	8.75	0.15
42	0.0	10.31	7.30	2.35	—	8.15	—	8.75	—	9.70	—	9.15	—
52	0.1	10.03	6.82	1.88	0.05	6.81	0.12	7.26	0.14	7.83	0.15	7.55	0.14

* σ = Standard deviation.

Metal titration : 5 ml 0.1 M $HClO_4$ + 5 ml 0.01 M metal solution + 4×10^{-3} M ligand + $NaClO_4$ solution + water.

The final volume in each set of titration was kept at 50 ml. Requisite amount of $NaClO_4$ solution was added in each set of titration to maintain the desired ionic strength.

Calculation : The proton-ligand formation constants ($\log K_n^H$) were obtained from the proton-ligand formation curves, plotting the $\bar{n}_H$ values[9] against pH values. The values were also obtained by point-wise calculation method[10] and agree closely. Only the mean values are given in Table 1.

From the ligand and metal-titration curves $\bar{n}$ and pL values were calculated.

Results and Discussion

Owing to the very low concentration of metal ions used in the present investigation, the formation of polynuclear complexation was considered to be unimportant. The metal curves showed departure from the ligand curve at pH much lower than the pH of hydrolysis of the metal ions[11,12] and this suggests that the liberation of proton is due to the chelation alone. The maximum values of $\bar{n}$ was ~0.7, which indicates 1 : 1 complexation beyond the region of metal hydrolysis. From the formation curves obtained plotting $\bar{n}$ *vs* pL the metal-ligand stability constant values ($\log K_1$) were obtained as pL values, where $\bar{n} = 0.5$. The log stability constant values were also calculated by the following expression

$$\log K_1 = \log \frac{\bar{n}}{1-\bar{n}} + pL \qquad (1)$$

The $\log K_1$ values along with the standard deviation (σ)[9] are shown in Table 1.

The stoichiometric metal-ligand formation constants determined at 42° and at three different ionic strength 0.01, 0.05 and 0.1 M ($NaClO_4$) were extrapolated to $\sqrt{\mu} = 0$ to get the respective thermodynamic values (Table 1). It is evident from Table 1 that the formation constants decrease with increase in ionic strength of the medium. This is in agreement with the observation made earlier[13,14].

It was observed that with decreasing temperature the stability constants show an increasing trend. This suggests that low temperature is favourable for complexation. The thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were also calculated and the values are reported in Table 2. The log K values reported here are accurate to ±0.3 log units and the values of ΔG, ΔH and ΔS are reliable to ±0.04 kcal mol^{-1}, ±0.5 kcal mol^{-1} and 2 cal mol^{-1} deg^{-1}, respectively.

The enthalpy terms, ΔH, are favourable for complexation as reflected by their negative values in all the cases. The entropy terms, ΔS, for the complexes, other than Pr^{III}, are negative and hence not favourable for complex formation. However, the free energy change, ΔG, for all the complexes are negative suggesting thereby that the complex formation is a spontaneous one.

TABLE 2—THERMODYNAMIC PARAMETERS OF THE METAL COMPLEXES WITH p-SUSASUD AT 42°

Cation	μ = 0.1 M $NaClO_4$			μ = 0 M $NaClO_4$
	−ΔG kcal mol^{-1}	−ΔH kcal mol^{-1}	ΔS cal mol^{-1} deg^{-1}	−ΔG° kcal mol^{-1}
Pr^{III}	9.96	4.68	+16.75	11.75
Nd^{III}	10.81	11.24	−1.37	12.61
Sm^{III}	11.73	14.52	−8.85	13.98
Gd^{III}	11.42	17.33	−18.78	13.19

Rare earths with their 4f orbitals being well shielded usually form ionic compounds and are expected to obey the Born relationship[15]. The log K_1 values when plotted against e^2/r show an increasing trend with a break at gadolinium. Certain amount of ionic character may, therefore, be suggested for the metal-ligand bonding although the possibility of some covalent interaction cannot be completely excluded[16].

The stability constants of the trivalent rare earth metal ions follow the order : $Pr^{III} < Nd^{III} < Sm^{III} > Gd^{III}$.

Such difference in the trend of stability constants is not uncommon in the case of lanthanides[17-19] and this may be traced to be due to the varying degree of stabilizations arising out of interactions of 4f metal orbitals with the ligand field[20].

References

1. C. R. BERA, S. CHATTOPADHYA and G. P. SENGUPTA, *J. Indian Chem. Soc.*, 1979, **56**, 416.
2. G. P. SENGUPTA and C. B. BERA, *J. Indian Chem. Soc.*, 1980, **57**, 516; 1980, **57**, 558; *J. Inorg. Nucl. Chem.*, 1981, **43**, 2139.
3. A. K. MUKHERJEE and P. RAY, *J. Indian Chem. Soc.*, 1955, **32**, 633.
4. A. I. VOGEL, "Quantitative Inorganic Analysis", Longmans, London, 1961, p. 239.
5. G. SCHWARZENBACH, "Complexometric Titrations", Methuen and Co., London, 1956, p. 60.
6. J. BJERRUM, "Metal Ammine Formation in Aqueous Solution", Haase, Copenhagen, 1941.
7. M. CALVIN and K. W. WILSON, *J. Am. Chem. Soc.*, 1945, **67**, 2003.
8. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
9. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
10. K. E. JABALPURWALA, K. A. VENKATACHALAM and M. B. KABADI, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1011.
11. T. R. HARKINS and H. FREISER, *J. Am. Chem. Soc.*, 1956, **78**, 1143.
12. H. T. S. BRITTON *Endeavour*, 1943, **2**, 150.
13. E. HÜCKEL, *Z. Physik.*, 1925, **26**, 93.
14. P. DEBYE, *Trans. Electrochem. Soc.*, 1942, **82**, 7.
15. R. A. ROBINSON and R. H. STOKES, "Electrolytic Solutions", Butterworths, London, 1959, p. 355.
16. T. MOELLER, D. F. MARTIN, L. C. THOMPSON, R. FERRUS, G. R. FEISTEL and W. J. RANDALL, *Chem. Rev.*, 1965, **65**, 1.
17. F. H. SPEDDING, J. E. POWEL and E. J. WHEELWRIGHT, *J. Am. Chem. Soc.*, 1956, **78**, 34.
18. J. SCHWARZENBACH and R. GUT, *Helv. Chim. Acta*, 1956, **39**, 1589.
19. R. C. VICKERY, *J. Mol. Spectrosc.*, 1956, **2**, 308.
20. L. K. A. STAVELY and T. RANDALL, *Faraday Discuss. Chem. Soc.*, 1958, **26**, 157.

Kinetics of Discharge of Zinc(II) and Nickel(II) Ions at the D.M.E. in Dithiodipropionic Acid

R. S. SAXENA*, (MISS) ALKA GUPTA and K. C GUPTA

Department of Chemistry, Malaviya Regional Engineering College, Jaipur-302 017

Manuscript received 30 September 1982, revised 7 January 1984, accepted 15 August 1984

THE electrochemical behaviour of several mercapto compounds and their metal complexes has already been studied[1-5] in these laboratories and yielded useful results. This communication reports the polarographic reduction of zinc and nickel in presence of dithiodipropionic acid, the determination of kinetic parameters under various experimental conditions and the values of change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the electrode reactions. The literature is, however, silent on these investigations.

Experimental

Dithiodipropionic acid (DTDPA) of 99% purity was supplied by Evan's Chemetics, New York. Zinc and nickel contents of zinc sulphate and nickel sulphate solutions were checked by estimating them as zinc pyrophosphate and nickel dimethylglyoximate. All other chemicals used were of AnalaR grade. Thymol was used as a maximum suppressor at a constant ionic strength ($\mu = 1$ *M*) maintained by $NaClO_4$.

C-V curves were drawn on a manual polarograph in an inert atmosphere of nitrogen using S.C.E. as the reference electrode with a thermostated H-cell. The capillary had the following characteristics : $m = 1.862$ mg sec^{-1}, $t = 3.66$ sec, $m^{2/3}t^{1/6} = 1.878$ $mg^{2/3}$ $sec^{-1/2}$ at $h_{Hg} = 50$ cms.

The current was recorded at the end of the drop-life instead of average current because the determination of kinetic parameters is based on Koutecky's method more accurately reproduced by measuring the maximum current[6].

Results and Discussion

The conventional log plots of the reduction waves of Zn^{2+} and Ni^{2+} in dithiodipropionic acid were straight lines but their slopes were not agreeing with the theoretical values indicating the irreversible nature of the waves in both the systems.

Effect of pH : Polarograms of 1 m*M* Zn^{2+} and Ni^{2+} in 0.04 *M* DTDPA and 1 *M* $NaClO_4$ were recorded in the *p*H range 1-7. It was observed that below *p*H 3.5 and above *p*H 5.5, the waves were not regular. However, a very well defined single cathodic wave was obtained at *p*H 4 where subsequent studies were carried out in both cases.

The values of half wave potentials in the case of Zn^{2+} and Ni^{2+} at *p*H 4 were -1.006 and -0.84, respectively. An examination of polarographic waves revealed that with increase in *p*H, the $-E_{1/2}$ displaced towards more negative potential showing the complex formation between Zn^{2+}/Ni^{2+} with DTDPA.

Effect of Hg pressure and temperature : The plots of i_d *vs* $\sqrt{h}$ (uncorrected) and temperature were found to be linear both in case of Zn^{2+} and Ni^{2+}.

The constancy of $i_d/h^{1/2}$ in each case and the values of temperature coefficients of i_d indicated the diffusion controlled nature of the waves.

Solutions of 0.04 *M* DTDPA and 1 m*M* Zn^{2+} and Ni^{2+} polarographed at temperatures 25, 30, 35, 40, 45 and 50° showed that the $E_{1/2}$ shifted to more positive values with the increase in temperature

TABLE 1—VALUES OF i_d, $E_{1/2}$, αn AND $k^{o}_{f,h}$ AT DIFFERENT CONCENTRATIONS OF DTDPA FOR 1m M Zn^{2+} AND Ni^{2+} SYSTEMS AT 30°

Concn. M	i_d (μA)		$-E_{1/2}$ V		αn		$k^{o}_{f,h}$ cm/sec^{-1}	
	Zn^{2+}	Ni^{2+}	Zn^{2+}	Ni^{2+}	Zn^{2+}	Ni^{2+}	$Zn^{2+}\times10^{-17}$	$Ni^{2+}\times10^{-7}$
0.02	16.28	14.52	1.002	0.837	1.355	0.615	0.051	0.770
0.04	15.48	13.96	1.006	0.84	1.290	0.553	0.136	1.49
0.06	14.92	13.39	1.009	0.844	1.231	0.483	0.443	4.49
0.08	14.88	12.92	1.011	0.848	1.178	0.455	1.42	5.82
0.10	13.47	12.35	1.013	0.853	1.129	0.430	4.24	7.43
0.12	12.98	11.98	1.015	0.858	1.084	0.410	12.10	8.71

TABLE 2—VALUES OF i_d, $E_{1/2}$, αn AND $k^{o}_{f,h}$ AT VARIOUS TEMPERATURES FOR 1m M Zn^{2+} AND Ni^{2+} SYSTEMS AT 0.04 M [DTDPA]

Temp. °C	i_d μA		$-E_{1/2}$ V		αn		$k^{o}_{f,h}$ cm sec^{-1}	
	Zn^{2+}	Ni^{2+}	Zn^{2+}	Ni^{2+}	Zn^{2+}	Ni^{2+}	$Zn^{2+}\times10^{-16}$	$Ni^{2+}\times10^{-6}$
25	14.34	13.3	1.008	0.844	1.062	0.437	10.40	2.05
30	15.48	13.96	1.006	0.84	1.106	0.444	8.29	1.85
35	16.22	14.71	1.003	0.836	1.153	0.451	0.978	1.81
40	16.98	15.47	1.001	0.831	1.178	0.463	0.582	1.58
45	17.73	16.41	0.996	0.826	1.231	0.475	0.147	1.39
50	18.68	17.17	0.990	0.821	1.290	0.488	0.037	1.20

(Table 1) showing the easier reduction of the complexes at elevated temperatures which is in accordance with the irreversible nature of the electrode process[7-8].

Effect of concentration of DTDPA : Polarograms of solutions containing different concentrations of DTDPA (0.02-0.12 M) and 1 mM Zn^{2+} and Ni^{2+} showed that with the increase in [DTDPA], the $E_{1/2}$ is displaced towards more negative potential and i_d decreases in each case indicating the complex formation between metal ion and DTDPA (Table 1).

Nature of complex : Since the polarographic waves were irreversible in both Zn^{2+} and Ni^{2+} ions, the classical method of Lingane[9] could not be used for studying the complex ion formation. Therefore, the method recommended by Tamamushi and Tanaka[10] was employed, using the following equation.

$$\frac{\Delta E_{1/2}}{\Delta \log C_X} = -q\,\frac{0.06014}{n\alpha}$$

Where α is the fraction of the total applied potential that favours the forward reaction and q is the number of ligands bound to the metal. The value of $n\alpha$ is obtained from the equation

$$E_{3/4} - E_{1/4} = \frac{-0.0574}{n\alpha}$$

The value of $\Delta E_{1/2}/\Delta \log C_X$ is determined from the slope of plots of log C_X *vs* $E_{1/2}$, where C_X is the concentration of the DTDPA. The value of q thus obtained works out to be approximately 1 in both the cases showing thereby that one mole of DTDPA combines with one mole of metal ion suggesting the formation of 1 : 1 complex between Zn^{2+}/Ni^{2+} and DTDPA.

Kinetic parameters : Since zinc and nickel reduce irreversibly at D.M.E. in presence of DTDPA, the values of transfer coefficient (α) and formal rate constant ($k^{o}_{f,h}$) for the electrode reactions have been determined under various conditions by Koutecky's method[11] as extended by Meites and Israel[12] using the following standard equations.

$$E_{d.e.} = E_{1/2} - \frac{0.0542}{\alpha n}\log\frac{i}{i_d - i} \qquad (1)$$

where

$$E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n}\log\frac{1.349\ k^{o}_{f,h}\ t^{1/2}}{D_o^{1/2}} \qquad (2)$$

The values of αn was obtained by equating the slope of $E_{d.e.}$ *vs* log $i/(i_d - i)$ plot to $-0.0542/\alpha n$ and the intercept of the same plot ($E_{1/2}$) was used to calculate $k^{o}_{f,h}$. The values of $D_o^{1/2}$ were determined from Ilkovic equation. The values of αn and $k^{o}_{f,h}$ at different concentrations of DTDPA and different temperatures are summarised in Table 1 and 2.

Thermodynamic parameters : The enthalpy of activation (ΔH) for the electrode reaction has been calculated by equating the slope of log $k^{o}_{f,h}$ *vs* 1/T plot to $-\Delta H/2.303R$ and found to be -31.89 and -2.080 kcal mol^{-1} for zinc and nickel systems, respectively.

The free energy of activation (ΔG) can be determined by expliciting the value of $k^{o}_{f,h}$ on the basis of general principles of the absolute rate theory

according to which

$$k^{o}_{f,b}=\frac{k\,T}{h}\,\phi\,\exp\left[\frac{-\Delta G}{RT}\right] \qquad (3)$$

Where k = Boltzmann constant, h = Plank's constant, $\phi = 2.0\times10^{-8}$ cm and other terms have their usual significance. From the equation (3), the values of ΔG for Zn^{2+} and Ni^{2+} systems are found to be 12.39 and 6.51 kcal mol^{-1}, respectively.

The entropy of activation (ΔS) calculated from the relation $\Delta S=(\Delta H-\Delta G)/T$, are found to be -146.15 and -28.37 cal mol^{-1} deg^{-1} for Zn^{2+} and Ni^{2+}, respectively.

References

1. R. S. SAXENA and K. C. GUPTA, *Can. J. Chem.*, 1968, **46**, 311.
2. R. S. SAXENA and U. S. CHATURVEDI, *J. Inorg. Nucl. Chem.*, 1972, **34**, 913.
3. R. S. SAXENA and P. SINGH, *Z. Naturforsch., Teil B*, 1969, **24**, 1520.
4. R. S. SAXENA and K. C. GUPTA, *Aust. J. Chem.*, 1968, **21**, 641.
5. R. S. SAXENA and S. S. SHEELWANT, *Indian J. Chem.*, 1973, **11**, 43.
6. L. MEITES, "Polarographic Techniques", Interscience, New York, 1955, p. 241.
7. R BRDICKA, *Collect. Czech. Chem. Commun.*, 1930, **2**, 489.
8. R. BRDICKA, *Collect Czech. Chem. Commun.*, 1931, **3**, 396.
9. J. J. LINGANE, *Chem. Rev.*, 1941, **29**, 1.
10. R. TAMAMUSHI and N. TANAKA, *Bull. Chem. Soc. Jpn*, 1949, **22**, 227.
11. J. KOUTECKY, *Collect. Czech. Chem. Commun.*, 1953, **18**, 597.
12. L. MEITES and Y. ISRAEL, *J. Am. Chem. Soc.*, 1961, **83**, 4903.

Hydrolysis of Esters in Slurry Phase Over Zinc Oxide Catalysts

V. KRISHNASAMY

A. C. College of Technology, Anna University, Madras-600 025

and

K. BALASUBRAMANIAN

Madras Institute of Technology, Anna University, Madras-600 044

Manuscript received 27 May 1983, revised 5 March 1984, accepted 10 August 1984

ESTER hydrolysis in heterogeneous systems using ion-exchange resins and mixed oxide catalysts are well known[1-4]. Zinc oxide has been reported to be effective in splitting oils and fats[5-7] in the preparation of fatty acids. This communication reports the kinetics of hydrolysis of aliphatic and aromatic esters over zinc oxide in slurry phase by conductivity method. The hydrolysis follows first order kinetics. Thermodynamic parameters are calculated for these reactions.

Experimental

Methyl acetate, ethyl acetate and methyl benzoate (A.R., B.D.H.) were purified by standard procedure[8] and their purity was checked by gas chromatography.

Catalyst A (ZnO) was prepared by adding ammonium hydroxide (A.R., B.D.H.) to a boiling zinc nitrate solution and the resulting zinc hydroxide precipitate was washed thoroughly and dried in an air oven at 120° for 12 h and then decomposed in a muffle furnace at 400° for 24 h. Catalyst B was obtained by the decomposition of zinc carbonate (A.R., B.D.H.) at 400° in a muffle furnace. Catalyst C was a commercial grade ZnO (B.D.H.). All samples were powdered and sieved to different mesh size and activated at 700° for 6 h by passing pure dry air through the sample and were cooled and preserved in a vacuum desiccator.

Procedure: 100 ml ester solution of known concentration was transferred into a 150 ml wide-mouthed bottle and a dip type conductivity cell was inserted into the solution. The arrangement was thermostated and kept over a magnetic platform. At the desired temperature known quantity of zinc oxide (100-120 mesh) was added to the system and the content stirred. Initial resistance (R_o), change in resistance at time t, (R_t) and at infinite reading (R_α) after 24 h were measured. The corresponding conductance values are σ_o, σ_t and σ_α. Initial ester concentration is equivalent to $(\sigma_\alpha-\sigma_o)$. Amount of ester hydrolysed or amount of acid formed is equivalent to $(\sigma_t-\sigma_o)$. Ester concentration at time t is equivalent to $(\sigma_\alpha-\sigma_t)$. After each experiment the catalyst was filtered, washed, dried and activated at 500° for 6 h by passing pure dry air.

Results and Discussion

The resistance remained constant with time when the experiment was performed (i) without ester, and (ii) without catalyst. In order to check the possibility of dissolution of the catalyst in water, the former was added to the latter, stirred for 1 h and filtered. No hydrolysis was observed when ester was added to the filtrate.

The resistance of acetic acid solution of known concentration remained constant before and after the addition of zinc oxide. This ensures that the observed resistance was only due to liberated acetic acid during hydrolysis and not due to the zinc acetate formation.

The effect of stirrer speed on the reaction rate was studied and the rate was found to be independent above 200 rpm. Since the kinetic studies were made at a stirrer speed of above 200 rpm, it is assumed that there is no diffusional effect.

The influence of particle size of catalysts A, B and C on the hydrolysis of methyl acetate was studied and the data are given in Table 1. Decrease

TABLE 1—EFFECT OF PARTICLE SIZE ON RATE CONSTANT

Catalyst	Rate constant; $k \times 10^3$, min^{-1}			
	100-120 mesh	72-100 mesh	52-72 mesh	36-52 mesh
A	3.428	2.572	1.687	1.213
B	2.558	1.863	1.186	0.948
C	1.740	1.142	0.835	0.552

in catalyst particle size results in an increase in the rate of hydrolysis. From these values, the activity of the catalysts is found to be in the following order: catalyst A > catalyst B > catalyst C.

The initial rates were obtained from Fig. 1 and from a log-log plot of initial rate *vs* initial concentration of methyl acetate (Fig. 2) the order of

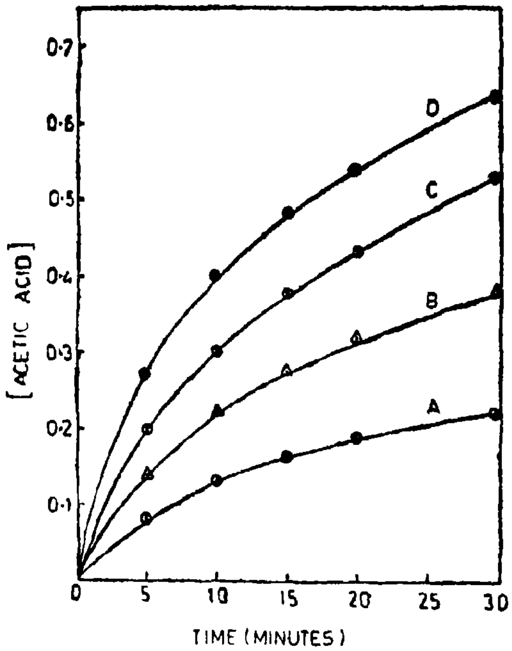


Fig. 1. Liberation of acetic acid from methyl acetate with time at 29° over catalyst A. A=0.378; B=0.63; C=0.881; and D=1.133 *M*.

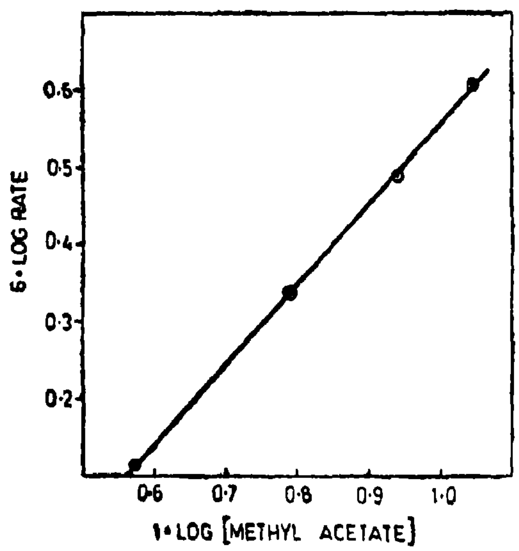


Fig. 2. Plot of log (initial rate) *vs* log (initial concentration) for methyl acetate. Temp. 29°.

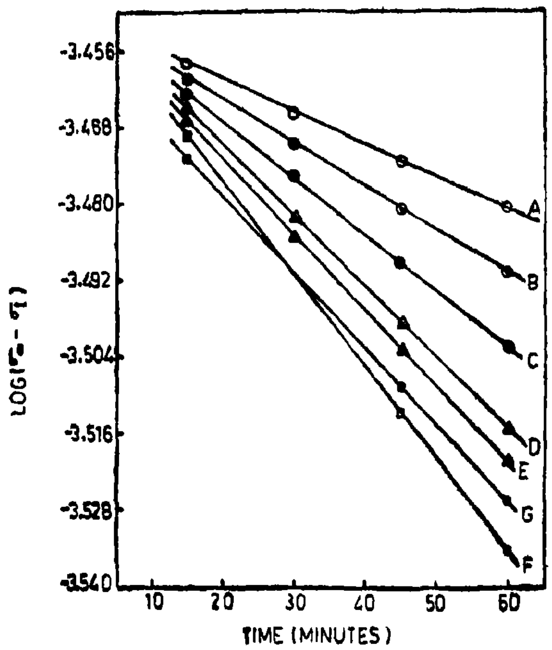


Fig. 3. Plot of log $(\sigma_\alpha - \sigma_t)$ *vs* time at 29° for methyl acetate over catalyst A. A=0.1; B=0.2; C=0.3; D=0.5; E=0.75; F=1.0; and G=1.5 g.

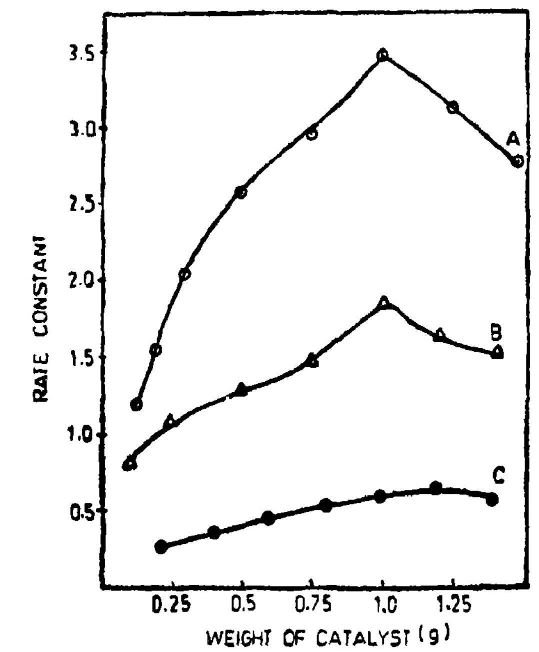


Fig. 4. Effect of catalyst concentration on rate constant for catalyst A at 29°. A=methyl acetate (0.503 *M*); B=ethyl acetate (0.5108 *M*); and methyl benzoate (0.56 *M*).

reaction was found to be 1.034. From the slopes of the plot (Fig. 3), the rate constants were calculated for methyl acetate over different amounts of catalyst A. Effect of catalyst concentration on rate constant for the three esters over catalyst A is shown in Fig. 4. It can be seen that the rate of

hydrolysis is in the following order : methyl acetate > ethyl acetate > methyl benzoate. The increase in the rate constant upto about 1.0 g (Fig. 4) may probably be due to the complete and uniform dispersion of the catalyst in the reaction vessel. Further additions beyond 1.0 g increase the bulk of the catalyst, but the ester molecules may not be able to reach the interior of the catalyst bulk and get adsorbed over the catalyst. Hence, the rates begin to fall.

The activation energy (E_a), frequency factor (PZ) and thermodynamic parameters ($\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$) for the three systems were calculated using Arrhenius and Eyring's equation[9] and the values are given in Table 2. The higher value of activation energy for methyl benzoate may be due to the precipitation of benzoic acid over zinc oxide.

TABLE 2—RATE CONSTANTS, FREQUENCY FACTOR AND ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF METHYL ACETATE, ETHYL ACETATE AND METHYL BENZOATE OVER CATALYST A

Temp. K	$k \times 10^4$, sec^{-1}	$PZ \times 10^{-3}$ sec^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ $JK^{-1}mol^{-1}$
		Methyl Acetate $E_a = 44.18$ kJ mol^{-1}			
302.0	5.746	2.514	41.672	98.540	−188.20
308.0	8.064	2.506	41.623	99.669	−188.50
314.0	11.171	2.494	41.573	100.800	−188.70
		Ethyl Acetate $E_a = 52.42$ kJ mol^{-1}			
303.5	3.090	32.45	49.901	100.60	−167.00
311.5	5.118	31.49	49.834	102.01	−167.50
319.5	8.251	30.63	49.567	103.43	−167.90
		Methyl Benzoate $E_a = 67.01$ kJ mol^{-1}			
303.5	1.068	3615	64.488	103.290	−127.84
313.5	2.506	3650	64.405	104.542	−128.02
323.0	7.942	3717	64.284	106.354	−128.26

References

1. C. W. DAVIES and C. G. THOMAS, *J. Chem. Soc.*, 1951, 1609.
2. R. VEDA, K. FUJIHARA and T. TERASHIMA, *J. Ferment. Tech. Jpn.*, 1956, **34**, 183.
3. S. A. BERNHARD and L. P. HAMMET, *J. Am. Chem. Soc.*, 1953, **75**, 1798.
4. S. P. WALVEKAR and A. B. HALGERI, *J. Indian Chem. Soc.*, 1973, **4**, 246.
5. A. E. BAILEY, "Industrial Oil and Fat Products", 1951, p. 805.
6. C. H. MARSEL and D. ALLEN, *Chem. Engg.*, 1947, **54**, 104.
7. A. K. GOPALAN, N. DESIKACHAR and M. V. A. IYENGAR, *Chem. Age (India)*, 1959, **10**, 577.
8. A. I. VOGEL, "A Text Book of Practical Organic Chemistry", Longmans Green, London, 1948.
9. S. GLASSTONE, K. J. LAIDLER and H. EYRING, "The Theory of Rate Processes", 1941, p. 197.

Conductometric Study of Interaction of Sodium *N*-Chlorobenzenesulphonamide with Silver(I), Mercury(II), Thorium(IV) and Zirconium(IV) Solutions**

B. N. USHA, RANGASWAMY* and H. S. YATHIRAJAN

Department of Post-graduate Studies and Research in Chemistry, Manasagangotri, Mysore-570 006

Manuscript received 5 November 1982, revised 16 March 1984, accepted 15 August 1984

IN continuation of our work on organic haloamines[1-3], we report in this note the result of our studies on the reactions of chloramine-B with some metal ions.

Experimental

Silver nitrate, mercuric chloride, thorium chloride, thorium nitrate, zirconium oxychloride and zirconium nitrate were of AR grade and their solutions were prepared in triply distilled water. Aqueous solutions of chloramine-B[1] were standardized by the iodometric method. All other chemicals used were of reagent grade.

Conductance measurements were made at room temperature (27°) using a Phillips PR 9500 conductivity bridge with a dip type conductivity cell (cell constant : 0.66 cm^{-1}). Potentiometric titrations were carried out on an Elico model LI-120 digital *p*H meter.

Uv spectra were obtained on a Beckmann DB spectrophotometer and ir spectra (KBr) were obtained on a Carl-Zeiss UR-10 spectrophotometer.

The white precipitates obtained by the addition of chloramine-B (CAB) to silver nitrate and mercuric chloride solutions were filtered, washed repeatedly with water, dried and analysed. The compound of Ag^{I} analysed for $C_6H_5SO_2NClAg$ (Found : Ag, 36.26 ; Cl, 11.73 ; S, 10.89 ; N, 4.65. Requires Ag, 36.18 ; Cl, 11.90 ; S, 10.72 ; N, 4.69%). The compound of Hg^{II} analysed for $(C_6H_5SO_2NCl)_2Hg$ (Found : Hg, 34.82 ; Cl, 12.48 ; S, 11.1 ; N, 4.85. Requires Hg, 34.5 ; Cl, 12.20 ; S, 11.01 ; N, 4.82%). Silver compound decomposed at 155-160° and mercury compound at 140°. Aqueous solutions of both the compounds liberate iodine from acidified potassium iodide solution.

The compound obtained by the addition of a solution of Th^{IV} or Zr^{IV} to a solution of CAB was filtered, washed with water and was estimated iodometrically in glacial acetic acid medium. The unreacted CAB in the filtrate was also determined iodometrically. The amount of H^+ reacted was calculated by titration against NaOH. It is found that CAB and H^+ reacted approximately in 1 : 1 molar ratio and the amount of product formed is nearly half the amount of CAB reacted. The solid

** Presented partly at the Annual Convention of Chemists, India, 1981.

obtained in the reaction of $ZrOCl_2$ melted at 74° and analysed for dichloramine-B (DCB or $RNCl_2$) (Found : Cl, 30.9 ; S, 14.21 ; N, 6.3. Requires Cl, 31.4 ; S, 14.16 ; N, 6.19%).

Results and Discussion

Conductivity titration curves of $AgNO_3$ and $HgCl_2$ with CAB have shown breaks at 1 : 1 and 1 : 2 molar ratios, respectively, in accordance with the composition in solid state. The stoichiometric equations can be represented as in (1) and (2).

$$RNClNa + AgNO_3 \rightarrow RNClAg + Na^+ + NO_3^- \quad (1)$$

$$2RNClNa + HgCl_2 \rightarrow (RNCl)_2Hg + 2Na^+ + 2Cl^- \quad (2)$$

where R is $C_6H_5SO_2$. The uv and ir spectra of CAB, RNClAg and $(RNCl)_2Hg$ are superimposable indicating that they are simple salts.

Similar conductivity titrations of thorium and zirconium solutions against CAB show breaks at 1 : 3 and 1 : 1 molar ratios, respectively. Carefully neutralised solutions of Th^{IV} and Zr^{IV} with NaOH were mixed with CAB, no precipitation was observed. These results indicate that H^+ produced, during the hydrolysis of these ions in aqueous solution is actually involved in the formation of DCB. The hydrolysis equilibria[4] of Th^{IV} and Zr^{IV} in aqueous solution can be represented by equations (3) and (4).

$$6Th(OH)_2^{2+} + 3H_2O \rightleftharpoons Th_6(OH)_{15}^{9+} + 3H^+ \quad (3)$$

$$Zr^{4+} + H_2O \rightleftharpoons Zr(OH)^{3+} + H^+ \quad (4)$$

The precipitate obtained could be dichloramine-B (DCB) which is only sparingly soluble in water. The breaks obtained at 1 : 3 and 1 : 1 molar ratios in conductometric titrations of Th^{4+} and Zr^{4+} with CAB probably indicate the formation of RNHCl. The disproportionation reactions of RNHCl has already been reported[1] and are shown in equations (5-7).

$$RNCl\,Na \rightleftharpoons (RNCl)^- + Na^+ \quad (5)$$

$$(RNCl)^- + H^+ \rightleftharpoons RNHCl \quad (6)$$

$$2RNHCl \rightleftharpoons RNH_2 + RNCl_2 \quad (7)$$

The uv and ir spectra of the precipitates and DCB prepared by literature method[5] were identical confirming the formation of DCB.

Acknowledgement

One of authors (B.N.U.) thanks the U.G.C., New Delhi for the award of a Senior Research Fellowship.

References

1. H. S. Yathirajan, Rangaswamy and D. S. Mahadevappa, *Collect. Czech. Chem. Commun.*, 1982, **47**, 1826.
2. Rangaswamy, H. S. Yathirajan and D. S. Mahadevappa, *Rev. Roum. Chim.*, 1981, **26**, 565.
3. Rangaswamy, B. N. Usha and H. S. Yathirajan, *Analyst*, 1984, **109**, 101.
4. D. S. Mahadevappa and Rangaswamy, *Indian J. Chem., Sect. A*, 1976, **14**, 463.
5. H. S. Yathirajan, D. S. Mahadevappa and Rangaswamy, *Talanta*, 1980, **27**, 52.

Intermolecular Attractive Forces at Oil/0.05% Lignosulphonate of *Eucalyptus tereticornis*-Water Interfaces

W. U. MALIK, S. K. SRIVASTAVA

Department of Chemistry, University of Roorkee, Roorkee

TRILOK CHAND*

Institute of Petroleum Exploration, Dehradun

and

SATISH KUMAR and A. K. JINDAL

Institute of Paper Technology, Saharanpur

Manuscript received 17 May 1983, revised 22 May 1984, accepted 15 August 1984

LITERATURE reveals that surface tension and interfacial tension are the direct measure of intermolecular forces, *viz*. spreading coefficient, liquid/liquid phase interaction, contact angles, Girifalco-Good's constants[1] *etc*. The attractive forces at oil/water interfaces between unlike molecules are mainly the dispersion forces[2-5]. The surface free energy on the surface layer depends upon the sum of attraction forces present on the surface molecules.

The molecular attraction calculations, between dissimilar molecules are the geometric mean of the despersion forces of the two sets of molecules. This comes directly from the original prediction of London[6] and is confirmed for different dissimilar molecules of equal size by studying regular solutions[7,8]. To evaluate the industrial use of any surface active agent, these parameters are the prerequisite and so the lignosulphonate of *Eucalyptus tereticornis* has been studied from this viewpoint and discussed systematically in this paper.

Experimental

Double-distilled kerosene (sp. gr., 0.7948), turpentine (sp. gr., 0.8745) and water having conductance $10^{-6}\ \Omega^{-1}\ cm^{-1}$ were used in all the experiments.

The alcohols, *viz*. methanol, ethanol, n-propanol, n-butanol pentanol and sodium chloride used were of AnalaR, B.D.H. grade. The lignosulphonate from eucalyptus wood was prepared at Star Paper Mills, Saharanpur and at Cellulose and Paper Branch, Forest Research Institute, Dehradun.

Surface tension : The surface tension, having various formulations of lignosulphonate concentrations, *viz*., 0.01, 0.02, 0.04, 0.08 and 0.1%, lignosulphonate 0.05%+0.1% v/v alcohols, lignosulphonate 0.05%+NaCl (0.01, 0.02, 0.04, 0.08 and 0.1%), and

lignosulphonate 0.05% at 20, 25, 30, 35 and 40°, has been reported by drop weight method[9,10].

Interfacial tension : The interfacial tension data of the above formulations against kerosene oil and turpentine oil have been used from the author's earlier work[11]. All the experiments were conducted at 25±1°.

Calculations of spreading coefficient, Girifalco-Good's constant and liquid/liquid interface interaction : The spreading coefficient, Girifalco-Good's constant, and liquid/liquid interface interaction of above formulations at kerosene and turpentine oil surfaces have been calculated from the following expressions, respectively[12]

$$S=\gamma_w-(\gamma_o+\gamma_{ow}) \qquad (1)$$

$$\gamma_{ow}=\gamma_o+\gamma_w-2\phi(\gamma_o\times\gamma_w)^{\frac{1}{2}} \qquad (2)$$

$$\text{Liquid/liquid interface interaction}=\gamma_{ow}^{cal}-\gamma_{ow}^{obs} \qquad (3)$$

where S is spreading coefficient ; γ_w, surface tension of aqueous phase ; γ_o, surface tension of oil phase ; γ_{ow}, interfacial tension ; ϕ, Girifalco-Good's constant ; γ_{ow}^{cal}, calculated interfacial tension ; and γ_{ow}^{obs}, experimental interfacial tension.

The results are presented in Tables 1-3.

TABLE 1—EFFECT OF LIGNOSULPHONATE CONCENTRATION ON INTERMOLECULAR FORCES

Lignosulphonate Concn. %	Kerosene oil S erg cm⁻²	Kerosene oil ϕ	Kerosene oil excess energy	Turpentine oil S erg cm⁻²	Turpentine oil ϕ	Turpentine oil excess energy
0.01	19.05	0.84	+19.05	23.40	0.87	+23.40
0.02	15.91	0.87	+15.91	22.41	0.93	+22.41
0.04	15.89	0.90	+15.89	21.53	0.96	+21.53
0.08	15.29	0.93	+15.29	20.10	0.97	+20.10
0.10	9.69	0.91	+ 9.69	14.44	0.95	+14.44

TABLE 2—EFFECT OF ALCOHOL-CARBON CHAIN LENGTH
Lignosulphonate concn.=0.05% (w/v)
Alcohol concn.=0.1% (v/v)

Alcohol	Kerosene oil S erg cm⁻²	Kerosene oil ϕ	Kerosene oil excess energy	Turpentine oil S erg cm⁻²	Turpentine oil ϕ	Turpentine oil excess energy
CH_3OH	25.70	0.96	+25.70	29.80	0.99	+29.80
C_2H_5OH	7.45	0.89	+ 7.45	10.95	0.91	+10.95
C_3H_7OH	20.90	0.82	+20.90	−17.85	0.82	+17.85
C_4H_9OH	25.55	0.91	+22.55	−22.40	0.89	−22.40
$C_5H_{11}OH$	28.35	1.01	−18.35	−25.20	0.98	−25.20

TABLE 3—EFFECT OF SALINITY
Lignosulphonate concn.=0.05% (w/v)

NaCl %	Kerosene oil S erg cm⁻²	Kerosene oil ϕ	Kerosene oil excess energy	Terpentine oil S erg cm⁻²	Terpentine oil ϕ	Terpentine oil excess energy
0.01	10.11	0.80	+10.11	14.94	0.88	+14.94
0.02	13.56	0.87	+13.56	19.66	0.92	+19.66
0.04	14.18	0.90	+14.18	19.63	0.95	+19.63
0.08	14.87	0.98	+14.87	19.25	0.97	+19.25
0.10	12.27	0.92	+12.77	17.49	0.96	+17.40

Results and Discussion

The results of spreading coefficients presented in Tables 1-3 show that higher lignosulphonate concentration and high temperature, lower the spreading coefficient and hence increase the spreading nature while higher salinity increases the non-spreading nature of aqueous phase containing lignosulphonate. Table 2 depicts that CH_3OH and C_2H_5OH favour spreading nature but for C_3H_7OH to $C_5H_{11}OH$, the spreading coefficient has negative values, thereby depicting a high cohesion and non-spreading nature.

Girifalco-Good's constant data show that higher concentration of lignosulphonate and salinity favour hydrogen bonding between oil and surfactant solutions while temperature disfavours this phenomenon. This is in agreement with the fact that for hydrogen bond formation in both the liquids, Girifalco-Good's constant must be greater than 0.84 value[1].

The calculated and observed interfacial tension data and liquid-liquid interaction (by assuming only dispersive force interactions at the surface) indicate that with the exception of C_3H_7OH to $C_5H_{11}OH$, γ_{ow}^{cal} is greater than γ_{ow}^{obs}, the excess energy may be attributed to the interaction between phases.

References

1 L. A. GIRIFALCO and R. J. GOOD, *J. Phys. Chem.*, 1957, **61**, 904.
2. F. M. FOWKES, *J. Phys. Chem.*, 1962, **66**, 1863.
3. F. M. FOWKES, *J. Phys. Chem.*, 1963, **67**, 2538.
4. F. M. FOWKES, "Adhesion", ASTM Spec. Tech. Pub., 1964, No. 360.
5. F. M. FOWKES, "Advances in Chemistry", 1964, 43, 99-111.
6. F. LONDON, *Trans. Faraday Soc.*, 1937, **8**, 33.
7. J. H. HILLDEBRAND and R. L. SCOTT, "Regular Solution", Practice-Hall, Anglewood Cliffs, 1962, pp. 79-80.
8. J. H. HILLDEBRAND and R. L. SCOTT, "Solubility of Non-electrolytes", 3rd ed., Reinhold, New York, 1950.
9. W. D. HARKINS and F. E. BROWN, *J. Am. Chem. Soc.*, 1913, **38**, 499.
10. W. D. HARKINS and F. E. BROWN, *J. Am. Chem. Soc.*, 1916, **41**, 228.
11. W. U. MALIK, S. K. SRIVASTAVA, T. CHAND and A. K. JINDAL, *J. Indian Chem. Soc.*, 1982, **59**, 1068.
12. F. M. FOWKES, *Ind. Eng. Chem.*, 1964, **40**, 12, 56.

Studies on Arndt-Eistert Synthesis : Synthesis of *N*-Aryl-*N'*-3-methylcaproylurea Derivatives

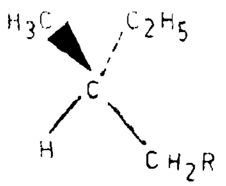
K. R. DESAI and M. M. PATHAK

Department of Chemistry, South Gujarat University, Surat-395 007

Manuscript received 15 February 1984, revised 24 May 1984, accepted 10 August 1984

UREA derivatives possess wide therapeutic activity such as antibacterial[1], antithyroid, hypnotic and anesthetic, hypoglycemic[2], anthelmintic, diuretic[3] and biocidal. Phenylacetamidourea derivatives are active anticonvulsants.

Arndt-Eistert[4] and Robinson and Bradley prepared diazoketones from acid chlorides with diazomethane. From this diazoketone various phenylurea derivatives were prepared. Optically active phenylurea derivatives were prepared to study whether optical activity remains or not. Optically active *S*-(−)-2-methylbutane-1-ol (**I**), $[\alpha]_D^{28}$ −4.62 (l=1) on bromination with red phosphorus and liquid bromine resulted in *S*-(+)-2-Me-1-bromobutane (**II**), $[\alpha]_D^{28}$+1.69 (l=1). It was then treated in ether with magnesium turnings, and carbon dioxide to give optically active *S*-(+)-2-methylvaleric acid (**III**), $[\alpha]_D^{30}$+4.66 (l=1). The acid chloride (**IIIa**) was obtained with thionyl chloride. Diazomethane was reacted with 2-methylvaleryl chloride to yield S-(+)-3-methylcaproic acid (**IV**), $[\alpha]_D^{28}$+4.75 which with thionyl chloride afforded *S*-(+)-3-methylcaproyl chloride (**IVa**), $[\alpha]_D^{28}$+4.88. The latter was condensed with different phenylureas to give optically active *N*-aryl-*N'*-3-methylcaproylureas (**V**).



I : R=OH ; II : R=Br ; III : R=COOH ; IIIa : R=COCl
IV : R=CH_2COOH , IVa : R=CH_2COCl;
and V : R=$CH_2CONHCONHR_1$.

Experimental

Infrared spectra (nujol) were recorded with a Beckman Model IR-5 spectrometer equipped with NaCl prism.

S-(−)-*2-Methylbutane-1-ol*[5] : Fusel oil contains as one of the constituents optically active *S*-(−)-2-methylbutane-1-ol which was obtained by fractional distillation, b.p. 126-28° ; $[\alpha]_D^{28}$ −4.62 (l=1) ; d_4^{28}, 0.8279 ; η^{28}, 1.450.

S-(+)-*2-Methyl-1-bromobutane* : A mixture of *S*-(−)-2-methylbutane-1-ol (440 g, 5 mol) and pure red phosphorus (31.06 g) was refluxed on a water bath and bromine (400 g, 129.2 ml) was introduced from a separating funnel into the mixture during 2 h at such a rate that there was always a little bromine vapour above the surface of the reaction mixture. The reaction mixture was further refluxed for 1 h and then distilled. Most of the bromobutane was collected at 112-22°. The latter was washed successively with water, an equal volume of conc. hydrochloric acid, and sodium bicarbonate solution (10%), and finally with water and dried with anhydrous calcium chloride. Redistillation at 116-18° gave the pure compound (57%) which was confirmed by tlc, $[\alpha]_D^{28}$+1.69 (l=1) ; d_4^{28}, 1.255 ; η^{28}, 1.455.

S-(+)-*2-Methyl-1-valeric acid* : In a three necked R.B. flask fitted with a mercury seal stirrer, reflux condensor and dropping funnel, were placed magnesium turnings (24.3 g), dry ether (300 ml) and also some iodine crystals. A solution of 2-methyl-1-bromobutane (151 g, 1*M*) in absolute dry ether was added from the dropping funnel. The reaction started after 3 min with disappearence of the iodine colour. The addition of bromobutane solution was continued dropwise at such a rate that the reaction did not become vigorous. Bromide in ether was added in 2 h and the reaction mixture was refluxed on warm water bath for 1 h.

Dry CO_2 gas was passed for 2-3 h below −5° and the whole mixture kept overnight. It was then decomposed by aqueous NH_4Cl solution (10%). The etheral layer was treated with aqueous NaOH (2*N*). The aqueous layer was acidified and extracted with ether. Etheral layer was dried over anhydrous magnesium sulphate and on evaporation the residual *S*-(+)-2-methylvaleric acid was purified by distillation at 197-98° (60%), $[\alpha]_D^{30}$+3.76 (l=1) ; d_4^{30}, 0.9636 ; η^{30}, 1.441.

S-(+)-*2-Methylvaleryl chloride* : In a R.B. flask thionyl chloride (1.5 mol) and *S*-(+)-2-methylvaleric acid (1.0 mol) were heated on a water bath for 0.5 h. *S*-(+)-2-Methylvaleryl chloride was distilled at 140-45° (80%), $[\alpha]_D^{30}$+2.65 (l=1 ; d_4^{30}, 0.9302 : η^{30}, 1.434.

Diazoketone[6] : In a R.B. flask containing the mixture of ether (500 ml) *S*-(+)-2-methylvaleryl chloride (2 g) and solution of diazomethane in ether was placed at 20-25° for 3-4 h. Ether was removed under reduced pressure. The residue was diazoketone.

S-(+)*3-Methylcaproic acid* : The diazoketone was mixed with dioxane (88 ml) and was treated with a mixture of silver oxide (2 g), anhydrous sodium carbonate (5 g), anhydrous sodium thiosulphate (3 g) in water (200 ml) and stirred at 55-60°. The temperature was raised to 90-100°, cooled, diluted with water and acidified to obtain *S*-(+)-3-methylcaproic acid. It was distilled at 208-9° (65%). The purity was checked by tlc (Found : C, 64.25 ; H, 10.19 and O, 24.09%) ; $[\alpha]_D^{30}$+4.21 (l=1) ; d_4^{30}, 1.0230 ; η^{30}, 1.417.

S-(+)-*3-Methylcaproyl chloride* : In a R.B. flask, thionyl chloride (1.5 mol) and 3-methylcaproic acid (1 mol) were refluxed for 0.5 h. *S*-(+)-3-Methylcaproyl chloride was distilled at 167-70° (57%) ; $[\alpha]_D^{30}$+4.01 (l=1) ; d_4^{30}, 0.9970, η^{30}, 1.404.

General method for preparation of optically active S-(+)-*3-methylcaproylurea derivatives* : A mixture of 3-methylcaproyl chloride (0.05 mol) and various phenylureas in ractified spirit was refluxed for 2 h. The cooled mixture deposited a solid which was washed with hydrochloric acid (2*N*) and then with water. The product was crystallized from ethanol.

Melting points of the compounds are mentioned below : R_1=phenyl, 135-36° ; *o*-tolyl, 155-56° ; *m*-tolyl, 115-16° ; *p*-tolyl, 160° ; *m*-nitrophenyl, 90° ; *p*-nitrophenyl, 133° ; *m*-chlorophenyl, 100° ; and *p*-chlorophenyl, 190°.

In these optically active phenylurea derivatives, the maximum rotation was found is the case of *N-m*-nitrophenyl-*N'*-3-methylcaproylurea, $[\alpha]_D^{30°}+110.5$ (l=1) and the minimum in the case of *N-m*-tolyl-*N'*-3-methylcaproylurea, $[\alpha]_D^{30°}+25.5$ (l=1).

Infrared spectra : All the compounds, in general gave the following bands : 1500-1480 (NH stretch), 1690-1570 (C=O stretch), -CO.NH.CO-stretching vibration 1640-1740 (CO.NH.CO stretch) and 710-690 cm^{-1}(CH stretch).

Antibacterial activity : The purified product was screened for antibacterial activity by cup-plate method using a species of gram-positive bacteria, *i.e. S. aureus* and a species of gram-negative bacteria, *i.e. E.coli*. Testing was carried out in ethanol solution at the concentration of 10 mg ml^{-1}.

The zone of inhibition of the test solutions were recorded.

The zone of inhibition against *S.aureus* was found maximum in the case of *N-o*-tolyl-*N'*-3-methylcaproylurea (8 m.m.) and minimum for *N-p*-tolyl-*N'*-3-methylcaproylurea (3 m.m.).

Similarly, for *E.coli* the maximum zone was found for *N-m*-chlorophenyl-*N'*-3-methylcaproylurea (5 m.m.) and minimum value occurred in the case of *N-p*-nitrophenyl-*N'*-3-methylcaproylurea ((2 m.m.).

Acknowledgement

Authors are thankful to South Gujarat University for providing facility and to U.G.C., New Delhi for awarding Junior Research Fellowship to one of the authors (M.M.P.).

References

1. R. H. WILLIAMS and E. G. FRAME, *Chem. Abstr.*, 1946, **40**, 54905.
2. H. FRANK and K. K. PATNAIK, *J. Indian Chem. Soc.*, 1950, **27**, 585.
3. W. L. LIPSCHITZ and E. STOKEY, *Chem. Abstr.*, 1945, **39**, 48955.
4. F. ARNDT, B. EISTERT and W. PARTIAE, *Chem. Ber.*, 1927, **60**, 1364.
5. E. L. BADIM and E. PASCU, *J. Am. Chem. Soc.*, 1944, **60**, 1963.
6. F. ARNDT and J. AMENDE, *Chem. Ber.*, 1928, **61**, 1122.

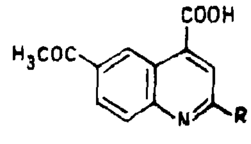
Studies on Chalcones : Preparation and Antimicrobial Activity of 2-Aryl-4-carboxy-6-acetylquinoline and 2-Aryl-4-carboxy-6-benzalacetoquinolines

D. J. BHATT, G. C. KAMDAR and A. R. PARIKH

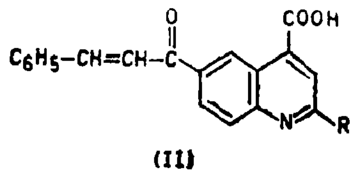
Department of Chemistry, Saurashtra University, Rajkot-360 005

Manuscript received 25 July 1983, revised 21 April 1984, accepted 16 August 1984

QUINOLINE derivatives possess wide therapeutic activity, *viz.* antiseptic[1], analgesics[2], tryphocidal[3], germicidal[4], antitubercular[5], anthelmintics[6] and antiserotonin[7]. Chalcones also possess anthelmintic[8], antimitotic and antimicrobial activity[10]. With a view to prepare better therapeutically active compounds, we have synthesised 2-aryl-4-carboxy-6-acetylquinoline of type (I)[11] and condensed them with benzaldehyde to get chalcones (II). The constitutions of acetoquinoline and chalcone were supported by ir spectra. The ir spectra (KBr) of 2-phenyl-4-carboxy-6-acetylquinoline and 2-phenyl-4-carboxy-6-benzalacetoquinolines showed bands at 1490 (C=N) and 1590 (C=C), 1360 (CH_3-CO) 1440 (COOH), and 1480 (C=N), 1590 (C=C), 1310 (CH=CH), 1670 (C=O) and 1440 cm^{-1} (COOH), respectively[12]. The products were screened for antibacterial activity.



(I)



(II)

where R = Aryl

Experimental

2-Aryl-4-carboxy-6-acetylquinoline : A mixture of purified benzaldehyde (0.01 mol), freshly distilled pyruvic acid (0.01 mol) and absolute ethanol (25 ml) was refluxed and a solution of *p*-aminoacetophenone (0.01 mol) in absolute ethanol (25 ml) was added slowly with frequent shaking. The mixture was further refluxed for 3 h and allowed to stand overnight. The product was filtered and crystallised from ethanol. The physical constants are recorded in Table 1.

2-Aryl-4-carboxy-6-benzalacetoquinolines : Benzaldehyde (0.01 mol) in ethanol (95%, 10 ml) was added to the mixture of 2-aryl-4-carboxy-6-acetylquinoline (0.01 mol) in ethanol (95%, 25 ml), aqueous sodium hydroxide (1%, 6 ml) and rectified spirit (95%, 10 ml) and stirred at 20-30° for 2-3 h. Content were then kept for 24 h at 0-10°, filtered and the product was isolated by acidification and crystallised from ethanol. The physical constants are recorded in Table 2.

Results and Discussion

Antimicrobial activity : The purified products were screened for antibacterial activity by cup-plate method[13] using a species of gram-positive bacteria, *i.e. Staphylococcus aureus* and a species of gram-negative bacteria, *i.e. Escherichia coli*. The testing was carried out in ethanol at a concentration of

TABLE 1—PHYSICAL CONSTANTS OF 2-ARYL-4-CARBOXY-6-ACETYLQUINOLINE (I)

Sl. no.	R	Molecular formula	M.p. °C	Yield	N% Found (Calcd.)	Diameter of zone of inhibition in mm (0.5 mg test solution)	
						S. aureus 24 h	E. coli 24 h
1	Phenyl	$C_{18}H_{13}NO_3$*	173-75	92	4.75 (4.81)	10	—
2	p-Anisyl	$C_{19}H_{15}NO_4$	125-27	82	4.40 (4.36)	40	—
3	o-Hydroxyphenyl	$C_{18}H_{13}NO_4$	192-94	83	4.56 (4.56)	40	15
4	m-Hydroxyphenyl	$C_{18}H_{13}NO_4$	164-66	86	4.40 (4.56)	44	—
5	p-Hydroxyphenyl	$C_{18}H_{13}NO_4$	157-59	81	4.40 (4.56)	40	—
6	3-Bromo-2-hydroxy-phenyl	$C_{18}H_{12}BrNO_4$	190-92	78	3.85 (3.63)	40	—
7	3,5-Dibromo-2-hydroxy-phenyl	$C_{18}H_{11}Br_2NO_4$	175-77	89	3.10 (3.01)	44	—
8	p-Nitrophenyl	$C_{18}H_{12}N_2O_5$	155-57	71	8.40 (8.33)	40	—
9	o-Chlorophenyl	$C_{18}H_{12}ClNO_3$	138-40	73	4.20 (4.30)	—	25
10	p-Chlorophenyl	$C_{18}H_{12}ClNO_3$	188-90	78	4.10 (4.30)	—	—

* Correct C, H analyses.

TABLE 2—PHYSICAL CONSTANTS OF CHALCONES (II)

Sl. no.	R	Molecular formula	M.p. °C	Yield	N% Found (Calcd.)	Diameter of zone of inhibition in mm (0.5 mg test solution)	
						S. aureus 24 h	E. coli 24 h
1	Phenyl	$C_{25}H_{17}NO_3$*	158-60	64	3.60 (3.69)	15	—
2	p-Anisyl	$C_{26}H_{19}NO_4$	95	56	3.40 (3.42)	22	10
3	o-Hydroxyphenyl	$C_{25}H_{17}NO_4$	110	54	3.51 (3.54)	12	15
4	m-Hydroxyphenyl	$C_{25}H_{17}NO_4$	195-97	60	3.50 (3.54)	28	10
5	p-Hydroxyphenyl	$C_{25}H_{17}NO_4$	147-48	61	3.48 (3.54)	20	—
6	3-Bromo-2-hydroxy-phenyl	$C_{25}H_{16}BrNO_4$	132-34	57	2.87 (2.95)	—	—
7	3,5-Dibromo-2-hydroxyphenyl	$C_{25}H_{15}Br_2NO_4$	105	53	2.48 (2.53)	—	—
8	p-Nitrophenyl	$C_{25}H_{16}N_2O_5$	300	54	6.40 (6.60)	15	—
9	o-Chlorophenyl	$C_{25}H_{16}ClNO_3$	153-55	50	3.25 (3.38)	40	—
10	p-Chlorophenyl	$C_{25}H_{16}ClNO_3$	198-200	51	3.22 (3.38)	40	—

* Correct C, H analyses.

10 mg ml^{-1}. *o*-Chlorophenyl and *p*-chlorophenyl derivatives of type (I) are highly active against *S. aureus* while *p*-anisyl, *o*-hydroxyphenyl and *m*-hydroxyphenyl are highly active against *E. coli*. *m*-Hydroxyphenyl, 3,5-dibromo-2-hydroxyphenyl of type II are highly active against *S. aureus*, while *o*-hydroxyphenyl and *p*-chlorophenyl derivatives are active against *E. coli*. This antimicrobial activity is less as compared to well known antibiotics like chloromycetin, penicillin, sulphadrugs, *etc*.

Acknowledgement

Authors are thankful to Saurashtra University for providing facilities and also thankful to C.S.I.R. and U.G.C., New Delhi for Junior Research Fellowships to two of us (D.J.B. and G.C.K.).

References

1. C. H. BROWNING, *J. Path. Bact.*, 1924, **27**, 121.
2. E, HESSE, *Arch. Exptl. Path. Pharmacol.*, 1930, 249.

3. C. H. BROWNING, *Proc. R. Soc. London*, 1932, 372.
4. K. MATSAMURA, *Bull. Agric. Chem. Soc. (Japan)*, 1926, 2, 159.
5. B. L. FREEDLANDEV, *Proc. Soc. Exptl. Biol. Med.*, 1952, 81, 66.
6. H. COLINE, S. African Pat., 68, 03, 686, 1968.
7. MIROSLAV, Czech Pat., 110, 130, 1964.
8. R. LALIBERTE, D. COMPBELL and C. BRUDORILEAN, *J. Pharm. Sci.*, 1947, 2, 37.
9. O. H. IVERSEN, *Nature (London)*, 1968, 219, 5149.
10. S. H. DANAGAONKAR and G. R. BAVANKEV, *Arch. Pharm. (Weinheim Ger.)*, 1967, 300, 697.
11. J. R. JOHNSON, *J. Am. Chem. Soc.*, 1921, 43, 2255.
12. K. D. GHUGE, P. UMAPATHY and D. N. SEN, *J. Indian Chem. Soc.*, 1978, 55, 864.
13. S. P. HIREMUTH, M. G. PUROHIT and M. SIRSI, *Karnatak Univ. J. Sci.*, 1974, 19, 203.

Synthesis of 3,5-Dimethyl-4-(substituted-sulfonamidobenzene azo, 4-sulfophenyl and 4-sulfonaphthyl azo)-1(*H*)-(hetero substituted) pyrazoles and Evaluation of Their Antibacterial Properties

P. S. FERNANDES*, DHIMANT DESAI,

(Miss) NEELAM GAWRI, SUDHANSHU PANDEY

and

HIMAT PATEL

Nadkarny-Sacasa Research Laboratories, St. Xavier's College, Mahapalika Marg, Bombay 400 001

Manuscript received 22 July 1983, revised 26 March 1984, accepted 10 August 1984

GREAT importance is being given to pyrazole derivatives due to their uses in therapeutics. Pyrazole compounds with 3- and 5-methyl group are found to possess hypoglycemic activity[1]. Isoxazole sulfa-drugs are stable substances and they are characterised by low toxicity and strong activity *in vivo* against bacteria[2]. Substituted-3(2*H*)pyridazinones are shown to possess antibacterial and antifungal activities[3].

In continuation of our work in pyrazole series[4], we wish to report the synthesis of few more compounds, *viz*. 3,5-dimethyl-4-(substituted sulfonamidobenzene azo, 4-sulfophenyl and 4-sulfonaphthyl azo)-1(*H*)-(hetero substituted)pyrazole compounds, and screening of their antibacterial properties.

Substituted sulfonamidobenzene azo, benzene azo-4-sulfonic acid and naphthalene azo-4-sulfonic acid derivatives of 2,4-diketopentane (acetylacetone) were prepared by coupling the 2,4-diketopentane with diazotised sulfonamido base, sulfanilic acid and naphthionic acid, respectively (**Ia**, **Ib**) in the presence of sodium acetate[5]. The azo derivatives of 2,4-diketopentane obtained was then reacted with four substituted carboxy hydrazides, *viz*. (*i*) 3,5-dimethyl-1(*H*)-(4-benzoyl hydrazide)pyrazole, (*ii*) 3,5-dimethyl-1(*H*)-(4-nitrophenyl)-4-(methyl carbhydrazide)pyrazole, (*iii*) 5-phenyl-3-(2-oxymethylene carbhydrazide)phenyl isoxazole, and (*iv*) 6-methoxy-2-(4-benzoyl hydrazide)-3(2*H*)pyridazinone, to furnish the corresponding *N*-substituted-3,5-dimethyl-4-(substituted sulfonamidobenzene azo)pyrazoles of the type **IIa** and *N*-substituted-3,5-dimethyl-4-(4-sulfophenyl azo and 4-sulfonaphthyl azo) pyrazoles of the type **IIb**. Hydrazones of the above carboxyhydrazides were also obtained by treating with the azo derivatives of 2,4-diketopentane.

Experimental

The sulfonamides were prepared by standard methods[6,7]. The azo compounds from 2,4-diketopentane were obtained in 48-75% yield by the method reported earlier[8]. The melting points were taken in open capillary and are uncorrected. The elemental analysis of all compounds (C, H, N and S) was found to be satisfactory.

3,5-Dimethyl-4-(substituted sulfonamidobenzene azo)pyrazoles: Equimolar quantities of the appropriate carbhydrazide was reacted with 2,4-diketo-3-substituted azo pentane in ethanol under reflux to give the corresponding hydrazones, which were crystallised from aqueous ethanol, and yields ranging from 70-85% (Table 1).

TABLE 1—HYDRAZONES FROM 2,4-DIKETO-3-(SUBSTITUTED SULFONAMIDOBENZENE AZO, 4-SULFOPHENYL AZO AND 4-SULFONAPHTHYL AZO)PENTANE

Sl. no.	X	R	M.p. °C
1	$HOOCCH_2-$	R_a	192
2	H_5C_6-	R_a	214
3	$4\text{-}NO_2-C_6H_4-$	R_a	217
4	$HOOCCH_2-$	R_b	178
5	H_5C_6-	R_b	106
6	$4\text{-}NO_2-C_6H_4-$	R_b	218
7	$HOOCCH_2-$	R_c	292
8	H_5C_6-	R_c	125
9	$4\text{-}NO_2-C_6H_4-$	R_c	208
10	H_5C_6-	R_d	254
11	$4\text{-}NO_2-C_6H_4-$	R_d	204
12	$4\text{-}SO_3H-C_6H_4-$	R_a	278
13	$4\text{-}SO_3H-C_{10}H_6-$	R_a	310
14	$4\text{-}SO_3H-C_6H_4-$	R_b	104
15	$4\text{-}SO_3H-C_{10}H_6-$	R_b	299
16	$4\text{-}SO_3H-C_6H_4-$	R_c	152
17	$4\text{-}SO_3H-C_{10}H_6-$	R_c	330
18	$4\text{-}SO_3H-C_{10}H_6-$	R_d	247

The above hydrazones were converted to the corresponding pyrazoles by refluxing it in glacial acetic acid. The same pyrazoles were also obtained by refluxing 2,4-diketo-3-substituted azo pentane with the respective carbhydrazide in glacial acetic acid for 8-10 h. The separated products were filtered and crystallised from ethanol with yields ranging from 45-75% (Table 2).

3,5-Dimethyl-4-(4-sulfophenyl azo and 4-sulfonaphthyl azo)pyrazoles: 2,4-Diketo-3-(4-sulfophenyl azo) pentane and 2,4-diketo-3-(4-sulfonaphthyl azo) pentane were prepared using the reported proce-

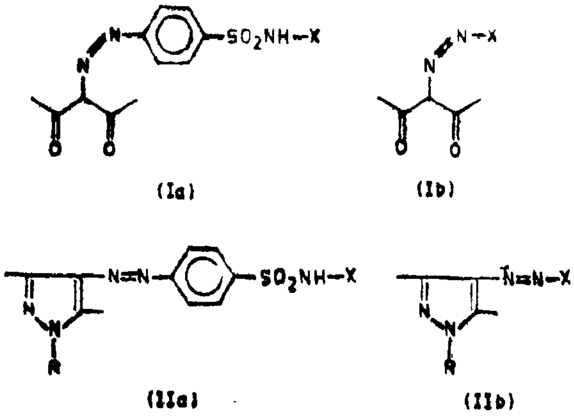
TABLE 2—3,5-DIMETHYL-4-(SUBSTITUTED SULFONAMIDOBENZENE AZO, 4-SULFOPHENYL AZO AND 4-SULFONAPHTHYL AZO)PYRAZOLE

Sl. no.	X	R	M.p. °C
1	$HOOCCH_2$ -	R_a	217
2	H_5C_6 -	R_a	194
3	4-NO_2 - C_6H_4 -	R_a	206
4	$HOOCCH_2$ -	R_b	108
5	H_5C_6 -	R_b	160
6	4-NO_2 - C_6H_4 -	R_b	111
7	$HOOCCH_2$ -	R_c	280
8	H_5C_6 -	R_c	166
9	4-NO_2 - C_6H_4 -	R_c	222
10	H_5C_6 -	R_d	166
11	4-NO_2 - C_6H_4 -	R_d	211
12	4-SO_3H - C_6H_4 -	R_a	292
13	4-SO_3H - $C_{10}H_6$ -	R_a	185
14	4-SO_3H - C_6H_4 -	R_b	267
15	4-SO_3H - $C_{10}H_6$ -	R_b	171
16	4-SO_3H - C_6H_4 -	R_c	205
17	4-SO_3H - $C_{10}H_6$ -	R_c	272
18	4-SO_3H - $C_{10}H_6$ -	R_d	286

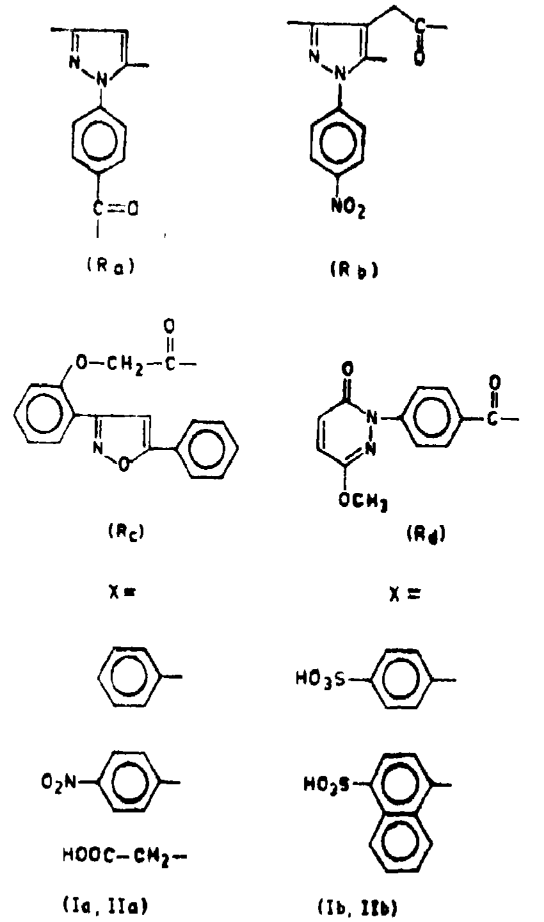
dure[5]. Azo dicarbonyl compounds were treated with the appropriate carbhydrazides using the procedure mentioned above, to obtain hydrazones (Table 1) and azo pyrazoles (Table 2), respectively.

Screening for antibacterial activity : The compounds in Table 2 have been evaluated for their antibacterial activity. The test organisms employed were *Bacillus subtilies, Staphylococcus aureus, Salmonella typhi, Escherichia coli,* and *Pseudomonas aeruginosa*. The antibacterial activity of the compounds were tested by ditch plate technique[8], using the concentration levels 2 mg and 3 mg per ml.

Compounds 1, 3 and 4 showed complete inhibition of *B. subtilies*. Compounds 12 and 16 showed complete inhibition of *S. aureus*. Compounds 12 and 16 showed complete inhibition of *S. typhi*, whereas compound 18 showed only partial inhibition. Compounds 14 and 16 showed complete inhibition of *P. aeruginosa*. The other compounds showed no activity on the organisms under study. None of the compounds studied showed any activity against *E. coli*. These results were identical for both the concentrations of the compounds studied.



Substituents R=R_a, R_b, R_c, R_d.



References

1. G. S. SAHARIA and H. R. SHARMA, *J. Indian Chem. Soc.*, 1974, **51**, 861.
2. K. KAWARA, Jap. Pat., 7669 1959 (*Chem. Abstr.*, 1954, **48**, 720).
3. T. TORIZO, T. MASAHIRO and D. YOSHIFUMI, *Yokugaku Zasshi*, 1969, **81**, 1617 (*Chem. Abstr.*, 1970, **72**, 55878).
4. P. S. FERNANDES, V. V. NADKARNY, G. A. JABBAR and B. P. JANI, *J. Indian Chem. Soc.*, 1975, **52**, 840.
5. P. S. FERNANDES, S. BHATE, G. PHILIP and V. V. NADKARNY, *J. Indian Chem. Soc.*, 1976, **53**, 830.
6. H. BAUER, *J. Am. Chem. Soc.*, 1939, **61**, 613.
7. R. O. ROBLIN, J. H. WILLIAMS, P. S. WINNEK and J. P. ENGLISH, *J. Am. Chem. Soc.*, 1940, **62**, 1999.
8. C. H. COLLINS and P. M. LYNE, "Microbiological Methods", 3rd ed., Butterworths, London, 1970, p. 424.

Reaction of Nitrosyl Chloride with Steroidal Olefins

SHAFIULLAH and M. RAFIUDDIN ANSARI

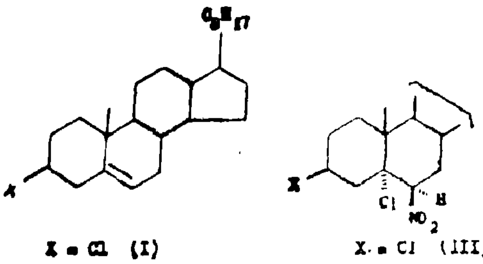
Steroid Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh-202 001

Manuscript received 16 December 1983, revised 18 June 1984, accepted 10 August 1984

NITROSYL chloride gas was used for chloronitrosation of steroidal alcohols[1] and oximes[2,3]. The work of Tanabe *et al.*[4] which dealt with the

action of nitrosyl chloride gas on some of the olefins prompted us to undertake an extension work in cholestane series.

This note reports the syntheses of 3β,5α-dichloro-6β-nitrocholestane (III) and 5α-chloro-6β-nitrocholestane (IV) when nitrosylchloride gas was passed in CCl_4 solution of 3β-chlorocholest-5-ene (I) and cholest-5-ene (II), respectively at 0°.



X = Cl (I) X = Cl (III)
= H (II) = H (IV)

Experimental

Nitrosyl chloride gas was prepared by the reported method[5].

3β-Chlorocholest-5-ene (I) (2 g) was dissolved in CCl_4 (100 ml) and cooled to 0°. Nitrosyl chloride gas was passed into the solution for 2 h. The solvent was evaporated under reduced pressure and the residue was dissolved in ether and washed with water, dried over anhydrous sodium sulphate and chromatographed over silica gel (40 g). Elution with petroleum ether-ether (40 : 1) gave compound 3β,5α-dichloro-6β-nitrocholestane (III) (1.5 g), crystallised from methanol, m.p. 111-113° (Found : C, 66.73 : H, 9.22 ; N, 2.81. $C_{27}H_{45}NO_2Cl_2$ requires C, 66.80 ; H, 9.27 ; N, 2.88%) ; *m/z* 485/437 (3 : 1) and 439/441 (3 : 1) ($M^+ - NO_2$) ; ν_{max} 1555, 1360 ($C-NO_2$) and 735, 720 cm^{-1} (C–Cl) ; δ ($CDCl_3$) 4.7 (dd, $C_6-\alpha H$, *J* 6.5 Hz and 3.3 Hz, equatorial), 3.9 (mc, C3–αH, $W\frac{1}{2}$ 18Hz, axial, A/B ring junction trans), 2.6 (d, C4–2H), 1.3 (s, C10–CH_3), 0.78 (s, C13–CH_3), 0.98 and 0.84 (other methyl protons).

Cholest-5-ene (II) (2 g) was dissolved in CCl_4 (100 ml) and cooled to 0°. Nitrosyl chloride gas was allowed to pass into the solution for 2 h. The solvent was evaporated under reduced pressure and the residue was dissolved in ether and washed with water, dried over anhydrous sodium sulphate and chromatographed over silica gel (40 g). Elution with petroleum ether-ether (20 : 1) provided 5α-chloro-6β-nitrocholestane (IV) (1.5 g), crystallised from methanol, gave positive Beilstein test, m.p. 91-93° (Found : C, 71.80 ; H, 10.14 ; N, 3.12. $C_{27}H_{46}NO_2Cl$ requires C, 71.84 ; H, 10.20 ; N, 3.10%) ; *m/z* 451/453 (3 : 1) and 405/407 (3 : 1) ($M^+ - NO_2$) ; ν_{max} 1553, 1355 ($C-NO_2$) and 720 cm^{-1} (C–Cl) ; δ ($CDCl_3$) 4.6 (dd, C6–αH, *J* 6.4 Hz and 3.2 Hz, equatorial) 1.25 (s, C10–CH_3), 0.72 (s, C13–CH_3), 0.96 and 0.82 (other methyl protons).

Results and Discussion

The compound (III), m.p. 111-113° was analysed for $C_{27}H_{45}NO_2Cl_2$. The ir spectrum exhibited bands at 1555, 1360 cm^{-1} ($C-NO_2$) and 735, 720 cm^{-1} (C–Cl). In nmr spectrum signal of C3-proton appeared at δ 3.9 ($W\frac{1}{2}$, 18 Hz, axial, A/B ring junction trans)[6]. C6 methine proton appeared at δ 4.7 (dd, *J* 6.5 Hz and 3.3 Hz, equatorial)[6], therefore, disposition of $C-NO_2$ bond is axial. A clear doublet at δ 2.6 integrated for two protons is ascribable to C4–2H. Mass spectrum corroborated the structure, which displayed weak molecular ion peaks at *m/z* 485/487 (3 : 1) and the diagnostic peaks at 439/441 (3 : 1) ($M^+ - NO_2$).

The compound IV, m.p. 91-93°, gave positive Beilstein test and analysed for $C_{27}H_{46}NO_2Cl$. The ir spectrum showed bands at 1553, 1355 ($C-NO_2$) and 720 cm^{-1}(C–Cl). The nmr spectrum displayed a double doublet at δ 4.6 integrated for one proton (*J* 6.4 Hz and 3.2 Hz) ascribable to C6–αH (equatorial). The structure was confirmed by mass spectrum which exhibited molecular ion peaks at *m/z* 451/453 (3 : 1) and 405/407 (3 : 1) ($M^+ - NO_2$).

Acknowledgement

The anthors are thankful to Prof. W. Rahman and Prof. M. S Ahmad for providing facilities and useful discussions. Financial assistance to one of the authors (M.R.A.) by C.S.I.R., New Delhi is gratefully acknowledged.

References

1. M. Akhtar and D. H R. Barton, *J. Am. Chem. Soc.*, 1962, **84**, 1496.
2. Y. Komeichi, S. Tomioka, T. Iwasaki and K. Watenabe, *Tetrahedron Lett.*, 1970, **53**, 4677.
3. E. Muller, H. Metzger, and D. Fries, *Chem. Ber.*, 1954, **87**, 1449.
4. K. Tanabe and R. Hayashi, *Chem. Pharm. Bull.*, 1962, **10**, 1177.
5. J. R. Morton and H. W. Wilcox, *Inorg. Synth.*, 1953, **4**, 48.
6. N. S. Bhacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry", Holden Day, San Fransisco, 1964, pp. 51-80.

Hentriacontan-12-ol and Other Waxy Constituents of *Tamarix gallica* Linn.**

C. K. ANDHIWAL and KAMAL KISHORE*

Research Laboratory, Chemistry Department, S. V. College, Aligarh-202 001

Manuscript received 3 October 1983, revised 29 March 1984, accepted 10 August 1984

TAMARIX gallica Linn, (Syn. *Tamarix troupii* Hole) commonly called *Jhau* belongs to family Tamaricaceae and is used in various ailments in Ayurvedic

** Presented in 185th. American Chemical Society National Meeting at Seattle, Washington, March 1983.

ystem of medicine[1,2]. Previously only 3,3'-dimethylether of ellagic acid[3], polyphenols[4], and phytosterols[5] have been isolated. In view of its medicinal values, a chemical study of the aerial parts of this shrub was undertaken and reported in this paper.

Results and Discussion

The aerial parts of *Tamarix gallica* Linn (900 g) after drying in air was ground and extracted thrice with petroleum ether (b.p. 60-80°) under reflux for 36 h. A dark greenish semi-solid extract (1.0%) was obtained which was neutral to universal indicator. The extract after usual workup was subjected to column chromatographic separation over activated alumina (40 fold excess) which gave different waxy fractions.

Fraction A : Elution with petroleum-ether (b.p. 60-80°) gave a waxy fraction (1.72 g) which showed two spots on tlc (silica gel, 2% $AgNO_3$) and therefore, was further resolved on a column of silica gel impregnated with 15% $AgNO_3$ and deactivated with 8% of water. Elution of the column with n-hexane and petroleum ether gave two products, respectively (Rf 1.0 and 0.87).

Product A : Hexane eluate on crystallisation from acetone-alcohol gave a waxy product (0.053 g), m.p. 53-55°. Its ir spectrum indicated the presence of alkanes with a long chain. It represented according to glc analysis the homologous series of n-alkanes $C_{18}-C_{35}$ (Table 1) with a maximum occurrence of n-hentriacontane (C_{31}, 25.21%), n-nonacosane (C_{29}, 14.68%) and n-heptacosane (C_{27}, 15.87%). Odd numbered homologue predominated over the even ones[6,7]. The distribution pattern of n-alkanes has been found to be of unimodal type[8].

TABLE 1—COMPOSITION OF n-ALKANES*

Sl. no.	No. of C-atoms	%
1	C_{18}	traces
2	C_{19}	0.10
3	C_{20}	0.41
4	C_{21}	0.62
5	C_{22}	1.05
6	C_{23}	1.54
7	C_{24}	2.09
8	C_{25}	3.81
9	C_{26}	8.24
10	C_{27}	15.87
11	C_{28}	9.47
12	C_{29}	14.68
13	C_{30}	6.81
14	C_{31}	25.21
15	C_{32}	5.07
16	C_{33}	4.59
17	C_{34}	0.98
18	C_{35}	0.25

* Glc analysis.

Product B : The second product was found of esters which showed prominent ir bands at 1170, 735 cm^{-1}. This product was then analysed by glc which represented the homologous series of long chain esters ($C_{40}-C_{52}$) (Table 2) with a maximum occurrence of C_{44} ester (32%). Even numbered esters were prevailing. However, odd numbered esters were also found in traces. The actual composition of fatty acids and alcohols in natural esters was not determined but according to results published earlier[9,10], it is supposed that single chromatographic peaks do not represent individual substances but mixtures of esters.

TABLE 2—COMPOSITION OF ESTERS*

Sl. no.	No. of C-atoms	%
1	C_{40}	3
2	C_{42}	5
3	C_{44}	32
4	C_{46}	17
5	C_{48}	19
6	C_{50}	5
7	C_{52}	3
8	unidentified	16

* Glc analysis.

Fraction B : Elution with petroleum ether-benzene (3 : 1) gave the fraction of secondary alcohols (0.196 g) which showed ir spectrum peaks at 1022, 1047, 1110, 1125, 1330 cm^{-1}. It was analysed by combined gas chromatography-mass spectrometry (GC–MS). The secondary alcohol consisted almost entirely of 12-hydroxy-hentriacontane (97%) with 1% each of C_{29} and C_{33} mixtures of homologue. C_{29} secondary alcohol has been found to be a mixture of 12–OH and 10–OH isomers showing characteristic mass fragmentation peaks at *m/e* 496 (M^+), 257 and 341 (12–OH isomer), 229 and 269 (10–OH isomer). C_{33} secondary alcohol has been composed of 12–OH and 14–OH isomers showing characteristic mass fragmentation peaks at *m/e* 552 (M^+), 257 and 397 (12–OH isomer), 285 and 369 (14–OH isomer).

It is worth mentioning here that the higher content of hentriacontan-12–OH, 97% of the total secondary alcohols, is unique findings in plants. Isolation of this unsymmetrical secondary alcohol has previously been reported only in Fragaria sp.[11], in which *ca.* 25% of 12–OH isomer was found in the mixture of secondary alcohols.

Fraction C : Further elution with petroleum ether-benzene (1 : 3) gave another fraction on crystallisation from methanol (0.1730 g), m.p. 84-85° and tlc homogeneous. The peaks in ir spectrum showed it an aliphatic long chain primary alcohol. It exhibited in mass spectrum the significant ions at *m/e* 438 (M^+), 437 (M^+-1), 420 (M^+-H_2O), 392 [$M^+-(olefin+H_2O)$], 45, 59, 73, 87 *etc.* Thus the primary alcohol was identified as n-triacontanol on the above basis and by preparation of its acetyl derivative, m.p. 67-68° (lit.[12] 69°). It was further confirmed when compared with the authentic specimen (co-tlc, m.m.p.).

Acknowledgement

The authors are grateful to Dr. S. C. Gupta, Principal, and Dr. M. Behari, Head of the Chemistry Department, S. V. College, Aligarh for providing facilities. Sincere thanks are due to Prof. A. P. Tulloch, National Research Council of Canada, Suskatchewan for glc and GC-MS analysis, and Lord Corporation, U.S.A. for ir spectra. Thanks are also due to U.G.C., New Delhi for the award of Junior Research Fellowship to one of the authors (K.K.).

References

1. K. R. KIRTIKAR and B. D. BASU, "The Indian Medicinal Plants", India, Vol. I, 1935, p. 247.
2. R. S. SINGH, "Vanoshadi Nidearshika", (Ayurvedic Pharmacopia), India, 1969, p. 162.
3. A. H. ISRAILI, R. C. SHARMA and A. R. KIDWAI, *Indian J. Chem.*, 1965, 3, 48.
4. G. CHAKRAVARTY, S. B. GUPTA and T. R. SESHADRI, *Indian J. Chem.*, 1965, 3, 171.
5. C. K. ANDHIWAL, K. KISHORE, T. ITOH and T. MATSUMOTO, *J. Natural Prod.*, 1982, 45, 222.
6. K. STRANSKY, M. STREIBL and V. HEROUT, *Collect. Czech. Chem. Comm.*, 1967, 32, 3215.
7. M. STREIBL, K. STRANSKY and V. HEROUT, *Collect. Czech. Chem. Comm.*, 1978, 43, 320.
8. S. HAMILTON and R. J. HAMILTON, *Top. Lipid Chem.*, 1972, 3, 199.
9. M. STREIBL, J. JIROUSOVA and K. STRANSKY, *Fette. Seifen. Anstrichm.*, 1971, 73, 301.
10. M. STREIBL, K. KONECNY, A. TRKA, K. UBIK and M. PAZLAR, *Collect. Czech. Chem. Comm.*, 1974, 39, 475.
11. E. A. BAKER and H. M. HUNT, *Phytochemistry*, 1979, 18, 1059.
12. "Dictionary of Organic Compounds", 2nd. ed., eds. I. M. HEILBORN and H. N. BUNBURY, Oxford University Press, 1953, Vol. IV, p. 588.

The Application of *p*-Amino-*o,o'*-dimethylazobenzene as Adsorption Indicator in Argentometry of Halides and Thiocyanate

D. C. AGARWAL, S. K. GARG and G. K. CHATURVEDI

Chemical Laboratories, Agra College, Agra-282 002

Manuscript received 18 January 1983, accepted 10 August 1984

As an extension of our earlier studies[1-3] investigations on the application of *p*-amino-*o-o'*-azobenzene in precipitimetry of halides (Cl^-, Br^- and I^-) and thiocyanate (SCN^-) using silver nitrate, have been made. The results of these investigations are presented in this communication.

Experimental

All the chemicals used were of A.R., B.D.H. or G.R., E. Merck grade. Stock solutions of halides, thiocyanate and silver nitrate were prepared in double-distilled water and standardised by usual methods. 0.2% solution of the dye was used (2-4 drops) as the indicator. The detailed experimental procedure has been described in our earlier communication[1].

In the argentometry of halides and thiocyanate, *p*-amino-*o-o'*-azobenzene dye is found to exhibit a sharp colour change from pink to yellow in the *p*H range 2-4.5. The indicator responded equally well in the reverse titration (Ag^+ *vs* halides) with a colour change from yellow to pink at the end point. The results are recorded in Tebles 1 and 2.

TABLE 1—TITRATIONS OF HALIDES AND THIOCYANATE USING *p*-AMINO-*o-o'*-DIMETHYLAZOBENZENE AS ADSORPTION INDICATOR WITH Ag^+ IONS*

Vol. of halide solution taken = 10.00 ml

Concn. of halide/ pseudohalide *M*	Vol. (ml), Concn. (*M*) of $AgNO_3$
0.1 KCl/KI	9.98-10.00, 0.1
0.1 KBr/KSCN	10.00-10.02, 0.1
0.02 KCl/KBr	10.00, 0.02
0.02 KSCN/KI	9.98-10.00, 0.02
0.01 KCl/KBr	9.98-10.02, 0.01
0.01 KI/KSCN	10.00-10.02, 0.01

* Titrations were conducted in presence of 2.0-4.0 ml 0.01 *M* HNO_3. The colour change yellow to pink was sharp and reversible. Coagulation of Ag-halide/thiocyanate occurred just at the end point.

TABLE 2—TITRATIONS OF Ag^+ IONS USING *p*-AMINO-*o-o'*-DIMETHYLAZOBENZENE AS INDICATOR WITH HALIDE/THIOCYANATE IONS*

Vol. of $AgNO_3$ taken = 10.00 ml

Concn. of $AgNO_3$ *M*	Vol. (ml), Concn. (*M*) halide/pseudohalide
0.1	9.98-10.00, 0.1 KCl/KSCN
0.1	10.00-10.02, 0.1 KBr/KI
0.02	10.00, 0.02 KCl/KSCN
0.02	10.00-10.02, 0.02 KBr/KI
0.01	9.98-10.00, 0.01 KCl/KBr
0.01	10.00-10.02, 0.01 KI/KSCN

* Titrations were performed in presence of 2.5-4.5 ml 0.01 *M* HNO_3. Coagulation of Ag-halide/thiocyanate occurred earlier and dye adsorbed on the coagulated particles, but at equivalence point desorption of the dye starts. Changes are sharp and reversible.

Determination of iodide in a mixture of chloride and iodide: The titration of iodide in a mixture of chloride and iodide was carried out using *p*-amino-*o-o'*-azobenzene. The mixtures containing varying concentration were taken. The solution was adjusted to *p*H 4 by adding requisite amount of 0.1 *M* HNO_3. Four drops of the dye solution were added to the solution which was titrated against standard solution of silver nitrate. At that *p*H only iodide was titrated and the results are shown in Table 3.

TABLE 8—DETERMINATION OF IODIDE IN A MIXTURE OF CHLORIDE AND IODIDE USING p-AMINO-o-o'-DIMETHYLAZOBENZENE AS INDICATOR*

Concn. of solution M	Vol. of KI+KCl ml	Vol. of $AgNO_3$ ml
0.1	10.00+10.00	10.05
0.2	10.00+10.00	10.00-10.02
0.01	10.00+10.00	10.02-10.04
0.05	10.00+10.00	10.00-10.02
0.1	5.00+10.00	4.98-5.02
0.2	5.00+10.00	5.00-5.02
0.01	7.00+10.00	6.98-7.08

* Titrations were performed at pH 4 where only I^- ions are titrated. The colour change yellow to pink was sharp and reversible and coagulation of AgX occurred near the end point

Results and Discussion

During the titration of halides thiocyanate by $AgNO_3$ using p-amino-o-o'-dimethylazobenzene as indicator, the colour change from yellow to pink at the end point is accompanied by a fall in pH from 4.05 to 3.60, which is more prominent in the case of iodide. The pH fall may be attributed to the deprotonation of the dye forming negatively charged dye ion. In the beginning AgX formed initially, is present in the medium containing abundance of halide ions. As the titration of X^- ions continues more and more AgX is formed and near the end point the amount of X^- ions is considerably reduced. These (X^-) are, however, adsorbed on the surface of AgX at active points having adsorbed Ag^+, forming weak mixed AgX-dye complex imparting a pink colour to the surface[8]. The colour changes in the reverse titration can similarly be explained.

Acknowledgement

The authors are grateful to Prof. J. P. Tandon, Rajasthan University for his valuable suggestions. Thanks are also due to Agra College authorities, and to C.S.I.R., New Delhi for awarding a Junior Research Fellowship to one of the authors (S.K.G.).

References

1. D. C. AGARWAL and G. K. CHATURVEDI, *J. Indian Chem. Soc.*, 1980, 57, 146.
2. S. K. GARG, D. C. AGARWAL and G. K. CHATURVEDI, *J. Indian Chem. Soc.*, in the press.
3. R. C. MEHROTRA and K. N. TANDON, *Anal. Chim. Acta*, 1962, 27, 17.

Dimethyldithiocarbamidohydrazine as an Extractive Spectrophotometric Reagent for Determination of Palladium(II) and Nickel(II) Individually and also from Their Binary Mixture

K. P. SENSARM, H. K. PAL and M. B. SAHA

Department of Inorganic and Analytical Chemistry, Jadavpur University, Calcutta-700 032

Manuscript received 25 January 1983, revised 24 May 1984, accepted 10 August 1984

THE utility of organic thio-ligands having nitrogen atoms in their molecules has been widely investigated by several workers[1-9]. Mention may be made of a few such reagents like thioamides, thioanilides, aminothiols, thiodiazoles, mercaptotriazoles, thiocarbamides and its various derivatives, aminothiocarboxylic acids, ruheanic acid, phenylhydrazine, sulfonic acid, *etc.* But their behaviour for the spectrophotometric determination of palladium and nickel, suffer from narrow pH range of extraction, variable composition of the complexs with variation of pH, interference from commonly associated metal ions, and difficulty of analytical separation of Pd^{II} and Ni^{II} from their binary mixture. All the above mentioned difficulties have been overcome in this present method of estimation of Pd^{II} and Ni^{II}. Moreover, the present reagent claims its superiority over the classical reagent, dimethylglyoxime for enabling the separation of Pd^{II} and Ni^{II}. The work involves the application of dimethyldithiocarbamidohydrazine[10] (METHALZIN), a newly introduced ligand, which can suitably be utilised for the spectrophotometric determination of Pd^{II} and Ni^{II} individually and also by separation from their binary mixture.

Methalzin forms a brown complex with Pd^{II} in aqueous solution within pH range 1.5-3.6, the complex being extractable in chloroform while the aqueous solution of Ni^{II} forms a brownish yellow complex with the reagent within pH range 7.5-9.6, the complex being equally soluble in chloroform. Thus by simply maintaining the proper pH of extraction, separation and determination of these two metal ions have been successfully achieved.

Experimental

Standard solutions of Ni^{II} and Pd^{II} : The metal ion solutions were prepared by dissolving known weights of AnalaR nickel chloride and palladium chloride in double-distilled water. The solutions were standardised by usual methods[11] using dimethylglyoxime.

Reagent solution : Dimethyldithiocarbamidohydrazine (METHALZIN) was prepared by the method[12] described earlier. As the excess amount of reagent has no adverse effect on absorbance. A 0.025% (w/v) solution of the reagent in absolute alcohol was used throughout the experiment. All other reagents and chemicals used were of AnalaR

quality. Chloroform used for extraction was purified by the recommended method.

All the absorbance measurements were made with the help of Spectromom 204 spectrophotometer and *p*H values were determined with Elico Model L 1-10 *p*H-meter.

Procedure :

Palladium(II) : A measured quantity of Pd^{II} solution was taken in a 50 ml separatory funnel to which 1 ml of 0.025% (w/v) reagent solution was added followed by requisite amount of 1 *N* sodium hydroxide solution so as to maintain the *p*H of the resulting solution within 1.5-3.6 in a total volume of 25 ml made up with water. The solution was shaken gently for 5 min. Extraction of Pd^{II} complex was made twice by adding 3 ml portions of chloroform at a time. The mixture was shaken vigorously each time for 5 min. The solvent layer after separation was transferred into a small beaker containing 0.5 g anhydrous sodium sulphate. Extractions of the Pd^{II} complex with 2 ml portions of chloroform were again made twice and the extracted Pd^{II} complex was collected into the same beaker. The combined extract was transferred into a 10 ml volumetric flask and diluted to the mark with the solvent. The absorbance of each solution was measured at 345 nm, the wavelength of maximum absorption, against reagent blank.

Nickel(II) : A known quantity of Ni^{II} solution was taken in 50 ml separatory funnel to which was added 1 ml of 0.025% (w/v) reagent solution. The *p*H of the solution was maintained between 7.5-9.6 by addition of 1*N* sodium hydroxide solution in a total volume of 25 ml made up with water. The brownish yellow Ni^{II} complex was extracted in 10 ml chloroform by the same procedure as already described in case of Pd^{II} complex. The absorbance of this solution was then measured at 340 nm, the wavelength of maximum absorption, against reagent blank.

Results and Discussion

The absorption spectrum of Pd^{II} complex has the maximum absorption at 345 nm whereas that of the Ni^{II} complex at 340 nm. But it is a matter of interest to note that the reagent has practically no absorption within the range of wavelength 340-345 nm. The absorption spectrum of the ligand in both the *p*H ranges of estimations of Ni^{II} and Pd^{II} at 7.5-9.6 and 1.5-3.6, respectively do not change.

A 0.025% (w/v) solution of the reagent in absolute alcohol was used for all measurements. Excess reagent has no adverse effect on the optical density of the solution.

The brown Pd^{II} complex was found stable in aqueous medium for 3 h even upto 60° and after extraction in chloroform the colour remains stable for more than 12 h at room temperature.

The brownish yellow Ni^{II} complex was found stable for more than 2 h in aqueous medium even above 40° whereas the chloroform extract was found stable for more than 8 h at room temperature.

Effect of pH : The optimum *p*H range for maximum development of colour of Pd^{II} complex was found to be between 1.5-3.6 and in case of Ni^{II} complex it was 7.5-9.6. This marked difference in the optimum ranges of *p*H helps to the separation and determination of these two metal ions from their binary mixtures.

Optimum range and photometric sensitivity and molar-extinction co-efficients : In the case of Pd^{II} complex Beer's law is obeyed within 1-7 ppm of Pd^{II}. The optimum concentration range as determined by Ringbom's [13] curve lies within 2.0-6.4 ppm of Pd^{II}, and the photometric sensitivity as per Sandell's definition was 0.0139 $\mu g/cm^2$. Beer's law was found to obey for Ni^{II} complex within the range 2.0-8.8 ppm of Ni^{II} whereas the optimum concentration range according to Ringbom's curve was 1.8-7.0 ppm of Ni^{II} and the photometric sensitivity according to Sandell's definition comes out to be 0.01205 $\mu g/cm^2$.

The molar extinction coefficient of Pd^{II} complex calculated from Beer's law was found to be 7650 $mol^{-1}cm^{-1}$, and that of Ni^{II} complex 4870 mol^{-1} cm^{-1}.

Precision and accuracy : The independent determinations containing 2.0 ppm of both Pd^{II} and Ni^{II} per 10 ml gave mean absorbance values 0.155 and 0.161, the standard deviations being 0.002 and 0.005 absorbance units, respectively.

Composition of the complexes : Ten stoichiometric composition of the complexes was determined by Job's method of continuous variation[14] and molar ratio method[15]. The result showed that Pd^{II} and Ni^{II} combined with the reagent in the ratio 1 : 1.

Effect of diverse ions : Fe^{III} is masked by NH_4HF_2 in case of Pd^{II} and Ni^{II}. Be^{II} does not interfere in the determinations in case of both the metal ions. La^{III} does not interfere in the determination of Pd^{II} but it does in case of Ni^{II}. Various common ions, *e.g.* Na^{I}, Ba^{II}, Sr^{II}, Ca^{II}, Mn^{II}, Cu^{II}, Mo^{VI}, Pt^{IV}, U^{VI}, Ga^{III}, Th^{IV}, Ru^{III}, Rh^{III}, Au^{III}, Os^{VI}, Re^{VII}, Ag^{I}, Cd^{II}, Zn^{II}, Hg^{II}, NO_3^-, Cl^-, SO_4^{2-}, oxalate, acetate, citrate and tartrate were tolerated in more than 100 times excess in case of Pd^{II}. Only cyanide ion interfere in determination of Pd^{II}. In case of nickel ions Ag^{I}, Bi^{III}, Hg^{II}, Co^{II}, Tl^{I}, citrate, cyanide and tartrate interfere seriously with the determination.

Determination of Pd^{II} and Ni^{II} by separation from their binary mixture : First to an aliquot of the mixture of acidic solutions of both the metal ions taken in a separatory funnel wes added 2 ml of 0.1% (w/v) reagent solution and the *p*H of the solution was maintained between 2-3 by adding requisite amount of 1*N* sodium hydroxide solution in a total volume of 10 ml made up with water. The Pd^{II} complex was then extracted in 10 ml chloroform in the usual way already described and the absorbances were

measured at 345 nm against the reagent blank. The aqueous layer remaining after the extraction of Pd^{II} complex, was treated with 2 ml of 0.1% (w/v) reagent solution and the pH of the mixture maintained between 8-9 with the help of 1*N* sodium hydroxide solution in a total volume of 25 ml made up with water. The Ni^{II} complex was then extracted in 10 ml chloroform according to the procedure already described and the absorbances of the nonaqueous layers were measured at 340 nm against the reagent blank. The results are shown in Table 1.

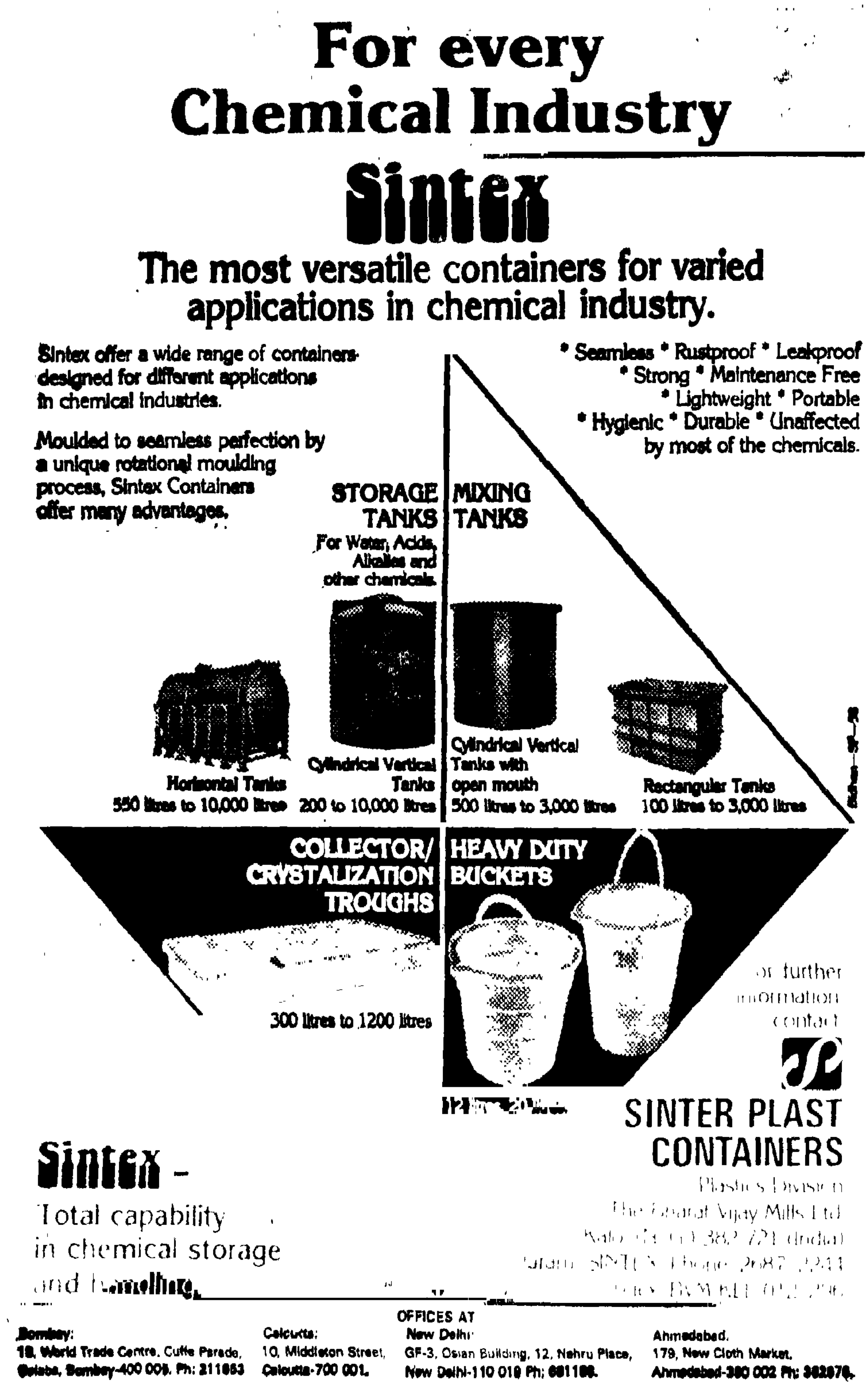
TABLE 1—DETERMINATION OF Pd^{II} AND Ni^{II} FROM THEIR BINARY MIXTURE

Amount of metal ions taken ppm	Pd^{II} found ppm	Ni^{II} found ppm
2.5 Pd^{II}	2.497	2.507
2.5 Ni^{II}		
3.0 Pd^{II}	3.011	3.510
3.5 Ni^{II}		
4.0 Pd^{II}	4.018	4.008
4.0 Ni^{II}		

References

1. J. GUPTA and B. CHAKRAVARTY, *J. Sci. Ind. Res.*, 1949, **8**, 133.
2. A. DUTTA AHMED and S. N. DHAR, *Sci. Cult.*, 1961, **37**, 207.
3. N. K. DUTTA and A. DUTTA AHMED, *Sci. Cult.*, 1962, **28**, 540.
4. N. K. DUTTA and K. P. SEN SARMA, *Sci. Cult.*, 1955, **20**, 397.
5. N. K. DUTTA and K. P. SEN SARMA, *Anal. Chim. Acta*, 1960, **23**, 531.
6. K. A. JENSEN and J. F. MIQUEL, *Acta Chem. Scand.*, 1952, **5**, 189.
7. A. DUTTA AHMED and P. K. MONDAL, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1633.
8. A. DUTTA AHMED and P. K. MONDAL, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2757.
9. P. N. DHAL, T. E. ACHARYA and A. NAYAK, *Indian J. Chem.*, 1975, **13**, 753.
10. H. K. PAL and K. P. SEN SARMA, Proceeding 68th Indian Science Congress, Part III, Section IV (Chemistry), **117**, p. 53.
11. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", 3rd ed., E. L. B. S., 1964, pp. 479, 511-512.
12. A. I. VOGEL, "A Text Book of Practical Organic Chemistry", 3rd ed., E. L. B. S., 1971, p. 176.
13. A. RINGBOM, *Z. Anal. Chem.*, 1949, **21**, 332.
14. P. JOB, *Ann. Chim. (Paris)*, 1928, **9**, 113.
15. A. E. HARVEY, JR. and D. L. MANNING, *J. Am. Chem. Soc.*, 1950, **72**, 1448.

J. Indian Chem. Soc.,
Vol. LXI, September 1984,



J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 827-829

Synthesis of Some Furan-2-aldoxime Complexes of Copper(II) Derived from Various Tetrathiocyanato-disubstituted Chromate(III) Ions

(Mrs.) P. R. SHUKLA, SURESH CHANDRA and SANJAY MISRA

Chemistry Department, Lucknow University, Lucknow-226 007

and

GOPAL NARAIN

Chemistry Department, University of Saugar, Sagar-470 003

Manuscript received 13 December 1982, revised 24 May 1984, accepted 20 September 1984

A series of the complexes of type $[Cu(FDH)_2][Cr(NCS)_4(L)_2]_2$ and $[Cu(FDH)_2][Cr(NCS)_4(L')]_2$, where FDH = furan-2-aldoxime, L = ammonia, aniline, *p*-toluidine, β- or γ-picoline, urea, thiourea, and L' = ethylenediamine, propylenediamine, *o*-phenanthroline and 2,2'-dipyridyl, have been prepared. The molar conductances of complexes in water (250 Ω^{-1}) indicate three ions. The sites of the coordination of various ligands to metal ions were decided with the help of spectral data (4000-400 cm^{-1}).

THE study of such complexes, in which both cation and anion are complex ions, is interesting as it provides an opportunity to study various configurations forced together in one complex moity. During the course of such a study some complexes of metal(II) nitroprussides and ferrocyanides were prepared and reported[1-3]. In the present paper we report the preparations and spectral data of a series of complexes of the type $[Cu(FDH)_2][Cr(NCS)_4(L)_2]_2$ or $[Cu(FDH)_2][Cr(NCS)_4(L')]_2$ where L=ammonia, aniline, *p*-toluidine, β- and γ-picoline, urea or thiourea, and L'=ethylenediamine (en), propylenediamine (pn), *o*-phenanthroline (phen) or 2,2'-dipyridyl (dipy). Conclusive evidence for the coordination of oxime to copper(II), and thiocyanate or other ligands to chromium(III) has been obtained from infrared spectral studies while the geometries of the complexes have been inferred by magnetic and electronic spectral data.

Experimental

The preparation of complexes involves four steps.

(i) *Furan-2-carbaldoxime*: The oxime was prepared by standard method using furan-2-carbaldehyde and hydroxylamine hydrochloride[4].

(ii) *Bisfuran-2-carbaldoxime copper(II) chloride*, $[Cu(FDH)_2]Cl_2$: Copper(II) chloride (13.35 g, 1 mol) suspended in methanol (100 ml) was treated with the oxime (22.2 g, 2 mol). The solution was refluxed for 6 h and the complex obtained was crystallised out by the repeated treatments with petroleum ether (b.p. 60-80°).

(iii) *Tetrathiocyanato-disubstituted chromate(III) salts*:

(a) *Compounds of type* $H^+[Cr(NCS)_4(L)_2]$: Anhydrous $K_3[Cr(NCS)_6]$ (5.21 g, 1 mol) was treated with either ammonia (0.321 g), aniline (1.86 g), *p*-toluidine (2.14 g) or picoline (1.86 g, 2 mol). Reactants were heated on a water bath for 3 h[5]. The compounds were precipitated out from the red coloured mass by adding acetic acid solution (20%), and crystallised with ethanol.

(b) *Compounds of type* $K[Kr(NCS)_4(L)$ *or* $(L')]$: Chrome alum (6.84 g), potassium thiocyanate (3.88 g) and either urea (1.20 g) or thiourea (1.52 g) in 1 : 4 : 2 molar ratio were dissolved in hot water. The mixture was evaporated slowly and the dried mass was extracted with ethanol[6]. The solution was concentrated when red-violet crystals were formed and recrystallised with ethanol. The same method was employed for ethylene or propylene diamine complex using 0.60 or 0.74 mol of the amine in accordance with 1 : 4 : 1 ratio.

(c) *Complexes of type* $K[Cr(NCS)_4(L')]$: Anhydrous $K_3[Cr(CNS)_6]$ (5.21 g, 1 mol) was dissolved in absolute ethanol (20 ml), and *o*-phenanthroline (1.52 g) or 1.34 g of 2,2'-dipyridyl (1.34 g, 1 mol) was added to the suspension, and the mixture was digested on a water bath for 2 h[7]. The solution was filtered out, concentrated and left overnight. Needle shaped pink crystals obtained were filtered and recrystallised with ethanol.

(iv) *Preparation of bisfuran-2-carbaldoxime copper(II)tetrathiocyanato-disubstituted chromate(III)*, $[Cu(FDH)_2][Cr(CNS)_4(L)_2$ *or* $(L')]_2$: The complex $[Cu(FDH)_2]Cl_2$ (3.55 g, 1 mol) was treated with any

uni-negative tetrathiocyanato-disubstituted chromate (III) salt (2 mol). The solution was strirred at room temperature for 2 h. The crystals of the new complex so obtained were filtered, washed, dried and analysed.

Copper and chromium were estimated gravimetrically as cuprous thiocyanate and barium chromate, respectively and thiocyanate was estimated volumetrically using standard silver nitrate solution[8]. Carbon, hydrogen and nitrogen were estimated microanalytically at C.D.R.I., Lucknow. The molar conductances were measured in water on Toshniwal CLOIO2A instrument. The ir spectra were recorded on Perkin-Elmer 577 spectrophotometer at C.D.R.I., Lucknow. Magnetic susceptibilities and electronic spectra were recorded at the Guru Nanak Dev University. The data are given in Table 1 and 2.

TABLE 1—ANALYTICAL DATA OF VARIOUS TETRATHIOCYANATO-DISUBSTITUTED CHROMATE(III) SALTS

Sl. no.	Compd.	Colour	Analysis % : Found/(Calcd.) Cr	NCS	C	H	N	λ (in water) Ω^{-1}	μ_{eff} B.M.
1.	$[C_6H_5NH_3^+][Cr(NCS)_4(C_6H_5NH_2)_2]$	Pink red	8.82 (9.22)	40.85 (41.13)	45.82 (46.80)	4.51 (3.90)	7.26 (7.44)	110	3.89
2.	$[p\text{-}CH_3C_6H_4NH_3^+][Cr(NCS)_4(p\text{-}CH_3C_6H_4NH_2)_2]$	Pink red	8.37 (8.28)	38.23 (38.28)	48.85 (49.50)	4.86 (4.62)	6.12 (6.93)	Insoluble	3.92
3.	$[\beta\text{-}CH_3C_5H_4NH^+][Cr(NCS)_4(\beta\text{-pic})_2]$	Pink	9.12 (9.22)	40.86 (41.13)	45.75 (46.80)	4.42 (3.90)	7.23 (7.44)	Insoluble	3.80
4.	$[\gamma\text{-}CH_3\text{-}C_5\text{-}H_4NH^+][Cr(NCS)_4(\gamma\text{-pic})_2]$	Pink	8.93 (9.22)	40.70 (41.13)	46.15 (46.80)	4.36 (3.90)	7.26 (7.44)	Insoluble	4.02
5.	$K[Cr(NCS)_4(urea)_2]$	Red	1 .67 (11.73)	51.03 (52.37)	15.93 (16.25)	2.83 (1.80)	12.56 (12.64)	128	3.92
6.	$K[Cr(NCS)_4(tu)_2]$*	Red	10.35 (10.99)	48.21 (48.84)	14.12 (15.15)	2.36 (1.68)	11.39 (11.78)	130	3.79
7.	$K[Cr(NCS)_4en]$	Red	13.17 (13.57)	60.26 (60.57)	18.15 (18.79)	2.86 (2.08)	6 93 (7.31)	126	4.21
8.	$K[Cr(NCS)_4pn]$	Red	11.12 (11.29)	49.20 (50.38)	22.88 (23.45)	2 83 (2.38)	20.98 (21.28)	120	4.08
9.	$K[Cr(NCS)_4(ophen)]$	Pink	9.63 (10.33)	45.70 (46.12)	37.44 (38.17)	2.51 (1.59)	5.34 (5.56)	Insoluble	4.10
10.	$K[Cr(NCS)_4(dipy)]$	Pink	10.22 (10.85)	47.93 (48.43)	52.83 (53.07)	2.37 (1.67)	5.12 (5.84)	Insoluble	3.82
11.	$NH_4[Cr(NCS)_4(NH_3)_2]$	Red	15.47 (14.93)	67.31 (68.52)	14.20 (14.28)	2.97 (3.78)	12 33 (12.50)	141	3.80

* tu - Thiourea.

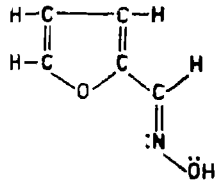
TABLE 2—ANALYTICAL AND MOLAR CONDUCTANCE DATA OF NEW OXIME COMPLEXES

Sl. no.	Complex	Colour	Analysis % : Found/(Calcd.) Cr	NCS	C	H	N	λ (in water) Ω^{-1}	μ_{eff} B.M.
1.	$[Cu(FDH)_2][Cr(NCS)_4(C_6H_5NH_2)_2]_2$	Brown	8.06 (8.49)	37.18 (37.87)	40.82 (41.14)	3.31 (3.10)	15.76 (16.00)	235	5.80
2.	$[Cu(FDH)_2][Cr(NCS)_4(p\text{-}CH_3C_6H_4NH_2]_2$	Brown	7.78 (8.12)	36 08 (36.22)	42.83 (43.09)	3.72 (3.59)	15.13 (15.30)	260	6.02
3.	$[Cu(FDH)_2][Cr(NCS)_4(\beta\text{-}C_6H_7M)_2]_2$	Yellow	8.12 (8.49)	37.12 (37.87)	40.89 (41.14)	3.34 (3.10)	15.83 (16.00)	Insoluble	5.68
4.	$[Cu(FDH)_2][Cr(NCS)_4(\gamma\text{-}C_6H_7N_2)_2]_2$	Yellow	8.08 (8.49)	37.20 (37.87)	40.72 (41.14)	3.36 (3 10)	15.78 (16.00)	Insoluble	5.95
5.	$[Cu(FDH)_2[Cr(NCS)_4(urea)_2]_2$	Yellow	9.13 (9.51)	41.81 (42.45)	24.05 (24.12)	2.71 (2.37)	22.56 (23.05)	Insoluble	5.90
6.	$[Cu(FDH)_2][Cr(NCS)_4(thiourea)_2]_2$	Yellow	8.29 (8.98)	40.00 (40.10)	22.26 (22.81)	2.64 (2.24)	21.23 (21.78)	260	5.82
7.	$[Cu(FDH)_2]]Cr(NCS)_4(en)]_2$	Yellow	9.81 (10.68)	47.30 (47.68)	27.10 (27.13)	3.10 (2.67)	19.04 (20.14)	255	6.31
8.	$[Cu(FDH)_2][Cr(NCS)_4(pn)]_2$	Yellow	9.86 (10.38)	46.15 (46.35)	28.12 (28.77)	3.72 (2.99)	19.15 (19.58)	Insoluble	6.25
9.	$[Cu(FDH)_2][Cr(NCS)_4(phen)]_2$	Yellow	8.13 (8.57)	37.82 (38.25)	40.48 (41.55)	2.75 (2.14)	15.78 (16.15)	225	6.08
10.	$[Cu(FDH)_2][Cr(NCS)_4(dipy)]_2$	Yellow	8.26 (8.92)	38.92 (39.82)	38.83 (39.14)	2.80 (2.23)	15.85 (16.82)	Insoluble	5.92
11.	$[Cu(FDH)_2][Cr(NCS)_4(NH_3)_2]_2$	Yellow	11.12 (10.29)	49.20 (50.38)	22.88 (23.45)	2.83 (2.38)	20.98 (21.28)	247	5.88

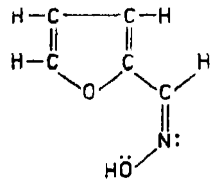
Results and Discussion

The analytical and molar conductance data suggest the molecular formulae of the complexes to be $[Cu(FDH)_2]\,[Cr(NCS)_4\,(L)_2$ or $(L')]_2$. The evidence for the coordination of ligands as FDH to copper(III) and thiocyanate, L or L′ to chromium(III) is obtained from the infrared data.

Ir spectra of β-furan-2-carbaldoxime : The ligand, furan-2-oxime can exist in two geometrical forms as shown below.



Sym or α-oxime



Anti or β-oxime

In the ir spectrum of free antioxime, two bands are observed at 3160 and 3040 cm^{-1} assigned to the intramolecularly bonded OH group, which are observed in complexes at 3360 cm^{-1}. The C=N stretching frequency in free oxime is observed at 1640 cm^{-1} which is shifted to 1660 ± 10 cm^{-1} in complexes, due to the increase in its bond order on coordination[9,10]. In free ligand, no band is observed below 700 cm^{-1}, while in complexes two distinct bands are seen at 670 and 510 cm^{-1} assigned to Cu-O (oxime) and Cu-O (furan ring) stretches[11-13]. These observations establish the coordination of oxime through oxime and furan ring oxygen atoms.

Ir spectra of other ligands : The coordination of thiocyanate ion through nitrogen and thiourea through sulfur is indicated by the presence of ν_{CN} at 2080 or 1500 cm^{-1} and ν_{C-S} at 748 or 750 cm^{-1}, respectively in the complexes[14-17].

In case of aniline, *p*-toludine, ethylene or propylene diamine complexes coordination of amine is inferred by the lowering of the ν_{NH} stretch which occurs at 3200 cm^{-1} in complexes[18-20]. The evidence for the coordination of *o*-phenanthroline and 2,2′-dipyridyl is obtained from the positive shifts in the position of C=C, C=N, ring stretchings ; C-H in plane deformation and ring breathing vibrations, which in free ligands occur at 1610, 1500, 1470 cm^{-1} and 1370, 1250, 1220 cm^{-1}, respectively[21-23].

All the complexes are highly paramagnetic in nature due to their spin-free configurations. The magnetic moments for various tetrathiocyanatodisubstituted chromium(III) salts (Table 1) around 3.89 B.M., correspond to the usual three unpaired electron value for chromium(III) ion, while the value for the copper complexes are very high (5.80 B.M.) due the four unpaired electrons of the two metal ions. Substracting the μ_{eff} value of the individual chromium(III) complex, gives resultant value around 1.90 B M. for the complexes which is the normal magnetic moment value for planar copper(II) complex ion. The characteristic d-d band of copper(II) (Cr^{III} bands being at 25.00, 19.00 and 13.50 kK) is observed at 15.40 kK, in the form of a broad band. The D_q values around 1540 cm^{-1} indicate that the oxime is a sufficiently strong ligand.

References

1. G. Narain, T. M. Agnihotri and P. R. Shukla, in the press.
2. G. Narain, A. M. Shakya and P. R. Shukla, in the press.
3. G. Narain, T. M. Agnihotri and P. R. Shukla, in the press.
4. O. L. Brady and R. F. Goldstein, *J. Chem. Soc.*, 1927, 1954.
5. M. A. Bennett, R. J. H. Clark and A. D. J. Goodwin, *Inorg. Chem.*, 1967, **6**, 1625.
6. G. Coutreas and R. Schimidt, *J. Inorg. Nucl. Chem.*, 1970, **32**, 127.
7. P. Pfeiffer and B. Werdelmann, *Z. Anorg. Allg. Chem.*, 1965, **235**, 263.
8. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", E.L.B.S., London, 1978, pp. 510, 453, 339.
9. K. Burger, "Coordination Chemistry Experimental Methods", Butterworth, London, 1973, p. 67.
10. K. Burger, *J. Inorg. Nucl. Chem.*, 1961, **27**, 2361.
11. R. A. Krause, *J. Phys. Chem.*, 1961, **65**, 2216.
12. G. Lees, *J. Chem. Soc. A*, 1971, 337.
13. K. Burger, R. Ruff and J. Ruff, *Acta Chim. Hung.*, 1960, **40**.
14. S. Guru, B. K. Mohapatra and B. Paul, *J. Indian Chem. Soc.*, 1977, **54**, 337.
15. I. Nakagawa and S. Mizushima, *Bull. Chem. Soc. Jpn.*, 1955, **28**, 589.
16. A. Yamaguchi, *J. Am. Chem. Soc.*, 1958, **80**, 527.
17. N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, 1958, 3478.
18. M. A. J. Jung Baur and C. Curran, *Spectrochim. Acta*, 1965, **21**, 141.
19. C. N. R. Rao and R. Venkatraghvan, *Can. J. Chem.*, 1966, **39**, 1757.
20. M. P. Coaklay, *Spectrochim. Acta*, 1965, **21**, 1984.
21. F. A. Cotton, D. D. Fant, D. M. L. Goodgame and R. H. Holm, *J. Am. Chem. Soc.*, 1961, **83**, 1780.
22. N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1960, 1130.
23. N. S. Gill, R. H. Nuthall, D. E. Scaife and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, 1961, **18**, 79.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 830-832

Mixed β-Diketonates of Copper(II) and Their Base Adducts

G. C. DASH and B. K. MOHAPATRA*

Department of Chemistry, B. J. B. College, Bhubaneswar-751 014

Manuscript received 9 December 1983, accepted 20 September 1984

Cu(bzac)$_2$ and Cu(dbm)$_2$ were reacted with an equimolar proportion of a number of other copper(II) β-diketonates (Cu L′), where L′ = dpm, hfac, tfac, tta or pta in dichloromethane, and mixed β-diketonates of the type (Cu LL′), where L = bzac or dbm, were isolated. Some of these mixed β-diketonates were reacted with pyridine to produce penta and hexacoordinated base adducts. These were characterised on the basis of analysis, molar conductance, magnetic susceptibility, and infrared and electronic spectral data.

THE chemistry of metal β-diketonates has aroused considerable recent interest[1] in such diverse areas as spectral studies, gas chromatography, solvent extractions[2], column and thin layer chromatography, nmr shift reagents, laser technology and as initiators in polymerisation reactions. Bis(β-diketonato) metal(II) complexes behave as Lewis acids and form five- or six- coordinate adducts with neutral donor molecules[4]. Stability of an adduct depends both on the basicity of the β-diketonate and on that of neutral ligand. Introduction of an electron withdrawing group, such as CF_3^- into β-diketone increases the affinity of central metal ion for ligation[5]. As a part of general programme on the reactions of transition metal β-diketonates, C[3] and C[1] bonded β-diketonates and complexes having β-diketonates as counter ions have been reported[6-9]. Also, C[3]-bonded hetero-β-diketones have been reported[10] showing the lability of the C[3]-bonded acetylacetonato moiety.

In continuation of this work, the present communication describes the mixed β-diketonates of copper(II) and their base adducts formed by reacting equimolar proportion of different copper(II) β-diketonates.

Experimental

All the chemicals used were of reagent grade. Different copper(II) β-diketonates were prepared from copper(II) acetate by earlier reported methods[11,12]. Equimolar mixture of Cu(bzac)$_2$ or Cu(dbm)$_2$ and other copper(II) β-diketonates, *i.e.* Cu(hfac)$_2$, Cu(tfac)$_2$, Cu(tta)$_2$, Cu(pta)$_2$, Cu(dpm)$_2$ were dissolved in 20 ml of dichloromethane and stirred magnetically at 40° for 20-30 min. Volume of the solutions were concentrated to 5 ml by a rotary vacuum evaporator and the samples were crystallised on slow cooling. The crystals were filtered, washed with small amount of ether and dried in vacuum. Copper was estimated iodometrically to determine the composition. The mixed β-diketonates were suspended in 3 ml pyridine and stirred magnetically for 20 min at 50-60°. The solutions were kept in refrigerator overnight and the crystalline compounds so obtained were filtered and dried in vacuum desiccator containing liquid paraffin. Copper and nitrogen were estimated by standard methods.

Conductance was measured in acetone solution (0.001 *M*) of the complexes using Toshniwal conductance bridge. Magnetic susceptibility measurements were made on solid specimens at room temperature by Gouy method. Infrared spectra (nujol) were recorded on Perkin-Elmer 621 and 337 spectrophotometers. Electronic spectra were recorded in dichloromethane solution (0.01 *M*) of the complexes using Unicam SP-500 spectrophotometer. All the relevant analytical data are presented in Table 1 and the spectral data in Table 2.

Results and Discussion

The complexes have the general composition [Cu(L)(L′)], where L is bzac or dbm and L′ is hfac, tfac, tta, pta or dpm, and the base adducts have the composition [Cu(L)(L′)py$_2$] or [Cu(L)(L′)(py)] (Table 1). These are green, olive green or blue crystalline solids having fairly low melting points and are soluble in common organic solvents, like ethanol, methanol, acetone, benzene, chloroform and dichloromethane. Acetone solution (0.001 *M*) of the complexes have low molar conductance values indicating non-electrolytic nature. Magnetic moment of the complexes indicate them to be paramagnetic with the presence of one unpaired electron as expected for the copper(II) ion. The base adducts of the mixed chelates are fairly stable in air unlike the adducts of bis(acetylacetonato)-copper(II) which loses the base on exposure to air.

Important infrared bands have been assigned and are listed in Table 2. Ir spectra of the mixed chelates and adducts do not exhibit any band due to free carbonyl group and also of free pyridine in the base adducts. There are two distinct sets of $\nu_{C=O}$ bands assignable[13] to L and L′ β-diketonate

TABLE 1—ANALYTICAL DATA OF MIXED β-DIKETONATES

Sl. no.	Compounds	Colour/form	M.p. °C	Λ_M $\Omega^{-1}cm^2$	μ_{eff} B.M.	Analysis % : Found/(Calcd. Cu	N
1.	Cu(bzac)(hfac)	Green/cryst.	132	8.5	1.81	14.95 (14.7)	-
2.	Cu(bzac)(tfac)	Blue/cryst.	115	6.2	1.79	16.5 (16.8)	-
3.	Cu(bzac)(tta)	Green/cryst.	198	10.1	1.82	14.56 (14.3)	-
4.	Cu(bzac)(pta)	Blue/cryst.	148	9.4	1.82	15.45 (15.15)	-
5.	Cu(bzac)(dpm)	Blue/cryst.	131	7.6	1.83	15.32 (15.6)	-
6.	Cu(dbm)(hfac)	Peagreen/cryst.	171	8.2	1.79	12.61 (12.87)	-
7.	Cu(dbm)(tfac)	Leaf green/cryst.	164	8.5	1.79	14.72 (14.46)	-
8.	Cu(dbm)(tta)	Green/cryst.	197	9.8	1.81	12.8 (12.52)	-
9.	Cu(dbm)(pta)	Olivegreen/cryst.	97	7.6	1.81	13.6 (13.2)	-
10.	Cu(dpm)(bzac)	Leafgreen/cryst.	218	9.4	1.80	13.9 (14.2)	-
11.	Cu(bzac)(hfac)py_2	Green/needles	120	8.6	1.82	10.52 (10.77)	4.42 (4.74)
12.	Cu(bzac)(tfac)py_2	Green/flakes	135	8.2	1.83	11.48 (11.86)	5.36 (5.22)
13.	Cu(dbm)(hfac)py_2	Green/crystal	158	7.8	1.81	9.44 (9.75)	4.38 (4.29)
14.	Cu(dbm)(tfac)py_2	Green/plates	142	8.8	1.82	10.82 (10.63)	4.41 (4.68)
15.	Cu(bzac)(dpm)py	Green/needles	146	9.8	1.83	13.31 (13.05)	2.66 (2.87)
16.	Cu(bzac)(tta)py	Green/crystal	156	6.5	1.82	12.35 (12.11)	2.54 (2.66)

bzac - anion of benzoylacetone, dbm - anion of dibenzoylmethane, dpm - anion of dipivaloylmethane,
hfac - anion of hexafluoroacetylacetone, tfac - anion of trifluoroacetylacetone,
tta - anion of thenoyltrifluoroacetone, pta - anion of pivaloyltrifluoroacetone.

TABLE 2—SPECTRAL DATA OF COMPLEXES

Compd. no.	Ir spectra (cm^{-1}) $\nu_{C=O}$ L	$\nu_{C=O}$ L'	ν_{Cu-O}	ν pyridine ring	Electronic spectra (nm) λ_{max} (ϵ)
1.	1580	1640	420	–	650 (35)
2.	1580	1615	425	–	650 (30)
3.	1585	1605	420	–	655 (30)
4.	1585	1610	430	–	650 (35)
5.	1580	1590	425	–	660 (35)
6.	1600	1630	420	–	660 (35)
7.	1605	1615	420	–	655 (30)
8.	1600	1605	425	–	650 (30)
9.	1600	1610	430	–	660 (35)
10.	1600	1580	430	–	660 (35)
11.	1600	1660	380	640	650 (50)
12.	1600	1625	385	645	650 (50)
13.	1610	1655	380	640	660 (55)
14.	1610	1625	390	635	655 (55)
15.	1600	1605	390	640	650 (80)
16.	1600	1620	380	645	655 (85)

moieties. Compared to the free β-diketones $\nu_{C=O}$ bands have been observed at considerably lower frequency regions in the mixed chelates. In the base adducts $\nu_{C=O}$ bands have shifted to the higher frequency region on coordination with the base[14], pyridine. Metal-oxygen stretching bands were assigned on the basis of the observations by Thornton *et al.*[15,16]. There are actually five metal sensitive bands in the far-infrared region. The least coupled M-O stretching band, ν_{Cu-O} was taken in this case as it shifts much on coordinations of the nitrogen ligand. In case of complexes under investigations ν_{Cu-O} shifts around 35-45 cm^{-1} to the lower frequency region in the base adducts compared to the parent mixed chelates and are observed at 380-390 cm^{-1}. Usually ν_{M-O} shifts to lower frequency in the base adducts, but this shift is quite large in case of copper(II) β-diketonates. This large decrease may be due to the repulsion effect and Jahn-Teller distortion taken together[17]. There are a number of bands in the far-infrared region for which it was difficult to assign ν_{Cu-N} in the base adducts. However, pyridine has the characteristic band at 605 cm^{-1} due to ring vibration (inplane ring deformation mode) and this band is much sensitive to coordinations and shifts to higher frequency region[18]. In the present case, the base adducts exhibit this band around 640-645 cm^{-1} region indicating coordination of pyridine.

Visible electronic spectra of the mixed chelates and the base adducts have been studied in dichloromethane solution. The mixed chelates give a broad absorption band at 650-660 nm with an ϵ value of 30-35. In case of the base adducts the band maxima does not shift much, but there is an increase in the intensity of the absorption band. In case of the bis-pyridine adducts ϵ values are around 50-55 whereas the monopyridine adducts have a very high in ϵ value, around 80-85. Graddon[4] and Walker[19] have observed[4,19-21] that in case of the base adducts an increase in the intensity of absorption band occurs without much shifting of the band maxima. To see that the monoadducts are truely 5-coordinated monomers rather than 6-coordinated dimers, the molecular weight of the compound [Cu(bzac)(dpm)py] was determined by vapour phase osmometric method in benzene. The observed molecular weight is 465.6 as compared with the calculated one, 486.54. This shows that the monoadducts are penta coordinated and bis-adducts are hexacoordinated.

Adducts of these copper(II) mixed β-diketonates are much stable than the adducts of bis(acetylacetonato)copper(II). This is obvious because when CH_3 group in acetylacetone is replaced by electron withdrawing group, the stability of the chelates decreases, at the same time however, the decrease of electron density around the central Cu^{II} ion enhances its ability to form adducts. Formation of the mixed β-diketonates indicates the lability of the copper(II) β-diketonates.

References

1. K. C. Joshi and V. N. Pathak, *Coord. Chem. Rev.*, 1977, **22**, 37.
2. W. R. Walker and N. C. Li, *J. Inorg. Nucl. Chem.*, 1965, **27**, 411; H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, 1965, **27**, 1359.
3. G. H. Bamford and D. J. Lind, *Proc. Roy. Soc. Ser. A*, 1967, 145; 1969, 302.
4. D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, 1961, **21**, 49.
5. R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1963, 5885.
6. B. K. Sahu and B. K. Mohapatra, *J. Indian Chem. Soc.*, 1981, **58**, 731.
7. B. K. Sahu and B. K. Mohapatra, *J. Indian Chem. Soc.*, 1982, **59**, 732.
8. B. K. Sahu, S. B. Mishra and B. K. Mohapatra, *Indian J. Chem., Sect. A*, 1982, **21**, 823.
9. B. K. Sahu and B. K. Mohapatra, *Indian J. Chem., Sect. A*, 1982, **21**, 186.
10. B. K. Sahu and B. K. Mohapatra, *Indian J. Chem., Sect. A*, 1982, **21**, 730.
11. A. Samantaray, P. K. Panda and B. K. Mohapatra, *J. Indian Chem. Soc.*, 1981, **58**, 408.
12. A. Samantaray, P. K. Panda and B. K. Mohapatra, *J. Indian Chem. Soc.*, 1983, **60**, 293.
13. D. P. Graddon, *Coord. Chem. Rev.*, 1969, **4**, 1.
14. F. Izumi, R. Kurosawa, H. Kawamoto and H. Akaiwa, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3188.
15. G. S. Shephard and D. A. Thornton, *Helv. Chim. Acta*, 1971, **54**, 2212.
16. G. C. Percy and D. A. Thornton, *J. Inorg. Nucl. Chem.*, 1973, **35**, 2719.
17. R. D. Hancock and D. A. Thornton, *J. Mol. Struct.*, 1969, **4**, 377.
18. K. Nakamoto "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, 1970, p. 212.
19. W. R. Walker and N. C. Li, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2255.
20. T. Shigmatsu, M. Tabushi, M. Matsui and M. Munnata, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2656.
21. P. E. Rakita, S. J. Kopperl and J. P. Fackler, Jr., *J. Inorg. Nucl. Chem.*, 1968, **30**, 2139.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 833-835

Some New Complexes of Indium(III) Salts with Acid Hydrazides

I. J. SALLOMI* and Z. F. DAWOOD

Department of Chemistry, College of Education, University of Mosul, Mosul, Iraq

Manuscript received 22 July 1983, revised 19 May 1984, accepted 20 September 1984

The complexes of the type $[In(LH)_3]X_3$, $[In(LH)_3X_3]$, $[In(LH)_2X]_2X$, $[In(LH)_2X_2]X$ and $[In(L)_3].2H_2O$ [where LH = the neutral molecules of benzoylhydrazine (BH, $C_6H_5CONHNH_2$), salicyloylhydrazine (SH, *o*-OH-$C_6H_4CONHNH_2$), paramethoxybenzoylhydrazine (PMBH, *p*-MeO-$C_6H_4CONHNH_2$) and paranitrobenzoylhydrazine (PNBH, *p*-NO_2-$C_6H_4CONHNH_2$), and X = Cl^-, Br^-, NO_3^-, SO_4^{2-}] have been prepared by reacting indium(III) salts with the suitable ligand and characterised by elemental analysis, infrared spectra and molar conductivity measurements.

Since the discovery of the antitubercular activity of acid hydrazides, many workers[1-9] have studied the coordination chemistry of these ligands.

These ligands contain different coordination centers and form two kinds of complexes. In neutral or slightly acidic medium, they act as neutral mono- or bi-dentate ligands forming cationic complexes, while in basic medium they act as monobasic bidentate forming neutral complexes[8,10,11]. As monodentate, they coordinate through either of their donor atoms[7,8,12,13].

In this paper the results of our investigation on the synthesis and characterisation of some new complexes of indium(III) with aroylhydrazines in both neutral and basic medium, are reported.

Experimental

Preparation of ligands : The ligands, benzoyl-, salicyoyl-, *p*-methoxybenzoyl- and *p*-nitrobenzoylhydrazines were generally prepared by the reaction of hydrazine hydrate with the corresponding ester according to the standard procedures[14-16].

Preparation of complexes : Several complexes of different types were isolated by the reaction of indium (III) salts with the ligands. In neutral medium, the reaction was carried out in alcoholic (ethanolic or methanolic) solutions in ~ 1 : 3 metal to ligand ratio (always 1 g metal salt was used with the corresponding amount of the suitable ligand). The reaction mixture was refluxed for ~1 h and then allowed to cool. In the basic medium, potassium hydroxide solution was added slowly to the mixture until complete precipitation of the complexes at *p*H 7-8.5. The isolated compound were filtered off, washed several times with cold alcohol followed by recrystallisation from ethanol and dried in a vacuum desiccator.

The complexes containing sulphate groups were prepared by fusion of 2 g indium(III) sulphate with 1.6 g benzoylhydrazine or 1.8 g salicyloylhydrazine (1 : 3 metal to ligand stoichiometry) at temperature slightly above the melting point of the ligands. The reacting mixture was cooled, followed by several times washing with ethanol, and dried in a vacuum desiccator to yield the products, benzoylhydrazine complex (1.55 g, 78%) and of salicyloylhydrazine complex (1.4 g, 66.6%).

TABLE 1—OBSERVED AND CALCULATED ANALYTICAL DATA

Compound	Analysis % : Found/(Calcd.)				
	C	H	N	X*	In
$In(BH)_3Cl_3$	39.86	4.03	13.13	16.51	18.27
	(40.12)	(3.82)	(13.37)	(16.72)	(18.31)
$In(BH)_3(NO_3)_3$	35.56	3.22	17.51	–	16.08
	(35.53)	(3.39)	(17.77)		(16.22)
$[In(BH)_2SO_4]_2SO_4$	31.75	3 05	10.42	9.41	21.40
	(31.64)	(3.02)	(10.55)	(9.04)	(21.66)
$In(SH)_3Cl_3$	37.01	3.63	12.21	16.11	17.30
	(37.22)	(3.55)	(12.41)	(15.66)	(16.98)
$In(SH)_3Br_3$	26 21	2.61	8.18	36.11	17.35
	(26.50)	(2.42)	(8.49)	(36.41)	(17.45)
$[In(SH)_2SO_4]_2SO_4$	29.63	2.95	10.14	8.52	20.62
	(29.84)	(2.84)	(9.95)	(8.35)	(20.43)
$In(SH)_3(NO_3)_3$	33.22	3.31	17.56	–	15.34
	(33.29)	(3.31)	(17.77)		(15.18)
$In(PMBH)_3Cl_3$	40.23	4.21	11.51	14.68	16.25
	(40.06)	(4.17)	(11.68)	(14.74)	(15.98)
$In(PMBH)_3Br_3$	28.18	3.07	8.40	35.21	16.44
	(27.95)	(2.91)	(8.15)	(34.93)	(16.74)
$In(PNBH)_3Cl_3$	33.30	2.86	16.58	14.06	15.2[illegible]
	(32.98)	(2.75)	(16.49)	(13.87)	(15.04)
$In(PNBH)_3Br_3$	28.19	2.46	14.16	26 82	12.67
	(28.06)	(2.34)	(14.03)	(26.77)	(12.80)
$In(BH)_3.2H_2O$**	45.21	4.71	14.93	–	20.35
	(45.32)	(4.50)	(15.11)		(20.68)
$In(SH)_3.2H_2O$**	42.16	3.62	14.21	–	19.31
	(41.93)	(3.66)	(13.98)		(19.12)
$In(PMBH)_3.2H_2O$**	44.72	4.91	13.18	–	17 65
	(44.58)	(4.80)	(13.00)		(17.80)
$In(PNBH)_3.2H_2O$**	36.62	3.31	18.45	–	16.46
	(36.47)	(3.18)	(18.23)		(16.64)

* X = Sulphur/ chlorine/ bromine.

** The same complexes were obtained by reaction of corresponding ligand with any of indium salts in alkaline medium or with indium hydroxide.

Elemental analysis: The isolated complexes were analysed for carbon, nitrogen, hydrogen, halogen, sulphur and indium by Alfred Bernhardt (West Germany) microanalyser. The analytical data are given in Table 1.

Physical measurements: Molar conductivity of the complexes in acetonitrile and dimethylformamide (DMF) at concentration $10^{-3}M$ were taken on an electrolytic conductivity measuring set model MC-1.

Ir spectra (KBr, nujol) were recorded on a Perkin-Elmer 557 spectrophotometer.

Results and Discussion

In cotinuation of our work[13,17,19], we prepared a number of complexes of indium(III) in both neutral and alkaline media.

In the preparation of the complexes in alcoholic solution always 1 : 3 complexes separated out even when excess of the ligands was used, while 1 : 2 complexes were obtained for indium bromide and indium sulphate. Analytical data (Table 1) show that the ligands form different types of complexes depending on the medium and the method of preparation. In neutral solution cationic and neutral complexes were obtained. In alkaline medium or by reaction with indium hydroxide, the ligands loses one proton to form deprotonated neutral complexes having 1 : 3 metal to ligand ratio, and usually one complex was separated out by the reactions of the different indium salts or indium hydroxide with the same ligand.

All the complexes are insoluble in water and most of the organic solvents, but they are slightly soluble in ethanol, dimethylformamide and acetonitrile. The cationic complexes melt in the range 95-230°, while the neutral complexes generally do not melt below 250° (Table 2). The neutral complexes are non-electrolyte. However, the molar conductivities of cationic complexes lying in the ranges 190-220. 140-150 Ω^{-1} mol^{-1} cm^2 in dimethylformamide and 110-130, 80-100 Ω^{-1} mol^{-1} cm^2 in ethanol, indicate 1 : 3 and 1 : 2 electrolytes (Table 2).

TABLE 2 – MELTING POINTS, AND MOLAR CONDUCTIVITIES (Ω^{-1} mol^{-1} cm^2) AT 25° OF 10^{-3} M SOLUTIONS IN DIMETHYLFORMAMIDE (DMF) AND ETHANOL

Compound	Λ_M (DMF)	Λ_M (ethanol)	M.p. °C
$In(BH)_3Cl_3$	220	128	92-94
$In(BH)_3(NO_3)_3$	194	116	237
$In(SH)_3Cl_3$	218	121	126-128
$In(SH)_2Br_3$	139	98	147-150
$In(SH)_3(NO_3)_3$	202	121	–
$In(PMBH)_3Cl_3$	211	124	146-148
$In(PMBH)_2Br_3$	146	112	136-138
$In(PNBH)_3Cl_3$	12	6	172-174
$In(PNBH)_3Br_3$	22	18	198-200
$In(BH)_3.2H_2O$	8	20	–
$In(SH)_3.2H_2O$	16	14	–
$In(PMBH)_3.2H_2O$	24	8	–
$In(PNBH)_3.2H_2O$	23	15	–

Infrared spectral data indicate that coordination in the complexes takes place in three different ways. (i) For complexes formed with benzoyl-, salicyloyl- and paramethoxybenzoylhydrazine in neutral solution, a negative shift of the order 15-28 cm^{-1} was observed for C=O stretching vibrations and a decrease of about 20-35 cm^{-1} in NH_2 bending frequencies. In addition the other NH_2 deformation vibrations located in the free ligands[22] at 950-1350 cm^{-1} are shifted to lower frequencies by the same order. While the positions of the bands due to NCO and OH deformation vibrations remain almost unchanged upon complex formation. These negative shift of C=O and NH_2 bands can be regarded as an evidence of coordination through both carbonyl oxygen and terminal hydrazide nitrogen atom. (ii) For complexes formed by reaction with *p*-nitrobenzoylhydrazine in neutral solution, the spectra of these complexes show negative shift of the order 25-40 cm^{-1} only in NH_2 bending vibrations, which indicate that the ligand coordinate only through the amino-nitrogen atom[13].

For complexes formed in alkaline solution also two different ways of coordination are indicated. (i) With the exception of salicyloylhydrazine complexes, in the spectra of the complexes formed with the other ligands, C=O stretching bands were absent. Instead two medium intensity bands appeared at 1320-1370 and 1600-1610 cm^{-1}, which are due to the stretching vibrations of C=O single and C=N double bonds, respectively (because of the conversion of the ligands to the enolic form in alkaline medium). The NH_2 deformation vibrations show a decrease of the order 20-35 cm^{-1}. Thus, coordination occurs through the enolic oxygen and the amino-nitrogen atoms. (ii) For SH complexes in the basic medium, the spectra indicate coordination through both imido-nitrogen (secondary amido nitrogen atom) and phenolic oxygen atoms, since the bands due to NCO deformation and OH stretching vibrations, present at 793 and 3500 cm^{-1}, respectively in the spectrum of the free ligand, were absent in the spectra of the complexes. This may support the above suggestion and indicate complexes with six-member ring structure.

In the spectra of the complexes, $In(SH)_2Br_3$, $In(PMBH)_2Br_3$, $In(PNBH)_3Cl_3$ and $In(PNBH)_3Br_3$, two bands in the low frequency region (260-295 cm^{-1}) are assigned to In-Cl and In-Br stretching vibrations, keeping in view their molar conductance.

Two complexes containing sulphate, $[In(BH)_2SO_4]_2SO_4$ and $[In(SH)_2SO_4]_2SO_4$ were prepared by fusing indium sulphate with the ligands in 1 : 3 molar ratio. The spectral bands at 1180, 1095, 1010 and 940 cm^{-1} are assigned to S-O stretching vibrations for the bridging bidentate sulphate[23]. In all the complexes, indium ion is six-coordinated with octahedral structure.

References

1. J. CYMERMAN-CRAIG, D. WILLIS, S. D. RUBBO and J. EDGAR, *Nature (London)*, 1955, 176, 34.
2. H. H. FOX "Chemotherapy of Acid-Fast Imfections" and in "Medicinal Chemistry", Ed., A. BURGER, 2nd Ed., Interscience, New York, 1960, pp. 982-984.
3. NG. PH. BUNN-HOI, NG. D. XUONG, NG. H. H. F. BINON and R. REGER, *J. Chem. Soc.*, 1953, 1358.
4. S. SORKIN, W. ROTH and H. ERLENMAYER, *Helv. Chim. Acta*, 1952. 35, 1736.
5. K. NAGANO, H. KINOSHITA and A. HIROKAWA, *Chem. Pharm. Bull.*, 1964, 12, 1198.
6. R. M. ISSA, M. F. EL-SHAZLY and M. F. ISKENDER, *Z. Anorg. Allg. Chem.*, 1967, 235, 90.
7. A. D. AHMAD and N. R. CHAUDURI, *J. Inorg. Nucl. Chem.*, 1971, 33, 189.
8. R. C. PAUL and S. L. CHADHA, *Spectrochim. Acta*, 1967, 234, 1249, 1249.
9. J. CHATT, J. R. DILWORTH, G. J. LEIGH and V. D. GAPTA, *J. Chem. Soc. (A)*, 1971, 2631.
10. M. F. ISKENDER, S. E. ZAYAN, M. A. KHALIFA and L. ELSAYED, *J. Inorg. Nucl. Chem.*, 1974, 26, 551.
11. A. ALBERT, *Experimentia*, 1953, 9, 370.
12. A. D. AHMAD, P. K. MANDAL and N. R. CHAUDHURI, *J. Inorg, Nucl. Chem.*, 1966, 28, 2951 ; 1969, 31, 2545.
13. I. J. SALLOMI and A. M. AL-DAHER, *J. Inorg. Nucl. Chem.*, 1979, 41, 1608.
14. T. CURTIUS and G. STROVE, *J. Prakt. Chem.*, 1894, 50, 295.
15. T. CURTIUS and O. TRACHMANN, *J. Prakt. Chem.*, 1895, 51, 165.
16. W. BAKER, C. N. HAKSAR and J. F. W. MCOMINE, *J. Chem. Soc.*, 1950, 170.
17. I. J. SALLOMI *J. Iraqi Chem. Soc.*, 1978, 3, 20.
18. F. R. AHMED, I. J. SALLOMI and Z. Y. AL-SAIGH, *J. Educt. Sci. (Iraq)*, 1980, 81.
19. I. J. SALLOMI and A. M. AL-DAHER, *J. Educt. Sci. (Iraq)*, 1980, 51.
20. N. K. DUTT and A. SENGUPTA, *J. Inorg. Nucl. Chem.*, 1971, 33, 4185.
21. YU. YA. KHARITONOV and R. I. MACHKHOSHVILI, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1971, 16, 604.
22. M. MASHIMA, *Bull. Chem. Soc. Jpn.*, 1962, 35, 1882 ; 1963, 36, 210.
23. K. NAKAMOTO, J. FUJITA, S. TANAKA and M. KOBAYASHI, *J. Am. Chem. Soc.*, 1957, 79, 4904.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 836-837

Binuclear Oxofluoro Complexes of Quinquevalent Molybdenum

M. C. CHAKRAVORTI and D. BANDYOPADHYAY

Department of Chemistry, Indian Institute of Technology, Kharagpur-721 302

Manuscript received 30 January 1984, revised 7 August 1984, accepted 20 September 1984

The non-electrolytic oxofluoro complexes, $Mo_2O_3L_2F_4$ (L=2,2′-dipyridyl and 1,10-phenanthroline) have been prepared from dilute HF medium which hydrolyse to Mo_2O_4-L_2F_2 on digestion with water. All the complexes are very weakly paramagnetic. Ir and the electronic spectra of the complexes confirm the presence of $Mo_2O_3^{4+}$ and $Mo_2O_4^{2+}$ moiety, respectively.

THE chemistry of quinquevalent molybdenum is dominated by its oxo complexes. The mononuclear paramagnetic complexes containing MoO^{3+} are successively dimerised to diamagnetic or very weakly paramagnetic oxo bridged species $Mo_2O_3^{4+}$ and $Mo_2O_4^{2+}$ as the acid concentration is decreased.

$$2MoO^{3+}+H_2O \rightleftharpoons Mo_2O_3^{4+}+2H^+$$

$$Mo_2O_3^{4+}+H_2O \rightleftharpoons Mo_2O_4^{2+}+2H^+$$

A few fluoro complexes containing the moiety $Mo_2O_4^{2+}$ have already been reported[1-3]. Only one complex, $Mo_2O_3(dipy)_2F_4$ containing the $Mo_2O_3^{4+}$ moiety has been reported[4]. The preparation of the complexes containing the $Mo_2O_3^{4+}$ moiety is somewhat difficult, since the intermediate $Mo_2O_3^{4+}$ in a reaction may undergo rapid hydrolysis to form $Mo_2O_4^{2+}$. Previous work in this laboratory showed that adding ligands to $K_2[MoOF_5]$ in neutral solution results in the formation of the complexes containing $Mo_2O_4^{2+}$ moiety directly[1]. In the present communication we report the formation of non-electrolytic fluoro complexes of the type $Mo_2O_3L_2F_4$ (L=2,2′-dipyridyl and 1,10-phenanthroline) from very dilute HF medium. The properties of these two types of complexes, *viz.* $Mo_2O_3L_2F_4$ and $Mo_2O_4L_2F_2$ have been compared.

Experimental

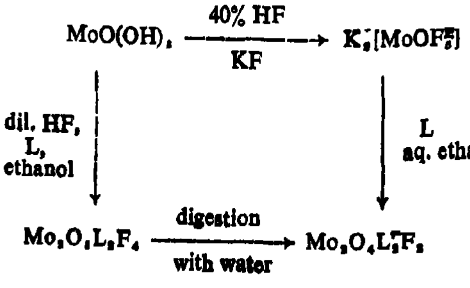
$MoO(OH)_3$ was prepared by standard method[5]. All chemicals used were of E. Merck / B.D.H., G.R./A.R. quality. Molybdenum was analysed by igniting the complexes to MoO_3. Nitrogen was determined by micro Dumas' method. The method of analysis of fluorine was described earlier[6].

Magnetic susceptibility was determined by Gouy method using $Hg[Co(NCS)_4]$ as calibrant. The diamagnetic corrections were taken from the standard sources[7]. Conductance was measured using a Systronics (BPL-India) 303 direct reading conductivity meter. Infrared spectra (KBr/CsI) were recorded on Perkin-Elmer 598 spectrophotometer. Reflectance spectra were recorded against MgO with a Carl Zeiss Jena VSU2-P spectrophotometer. Thermogravimetric analysis was carried out by the method described earlier[6].

$Mo_2O_3(dipy)_2F_4$ and $Mo_2O_3(phen)_2F_4$: A solution of 2,2′-dipyridyl (0.95 g, 0.006 mol) or 1,10-phenanthroline monohydrate (1.2 g, 0.006 mol) in HF (40%, 2 ml) was added to a solution of $MoO(OH)_3$ (1.0 g, 0.006 mol) in HF (40%, 3 ml). Ethanol (50 ml) was added to the solution with constant stirring. The deep violet precipitate appeared after 5 min which was separated after 0.5 h, washed with ethanol and dried in vacuum over concentrated H_2SO_4. The yields were about 0.25 g and 0.2 g respectively.

$Mo_2O_4(dipy)_2F_2$ and $Mo_2O_4(phen)_2F_2$: The compounds $Mo_2O_3(dipy)_2F_4$ and $Mo_2O_3(phen)_2F_4$ were digested with water for 1 h. The deep violet colour changed to reddish brown. The residues were washed with water and then with ethanol. The yields were almost quantitative.

These two compounds were earlier prepared[1] from $K_2[MoOF_5]$. The formation of all the compounds from $MoO(OH)_3$ is shown in Scheme 1. The analytical data are given in Table 1.



Scheme 1

TABLE 1—ANALYTICAL DATA

Compound	Analysis % : Found/(Calcd.)			$\Omega^{-1}mol^{-1}$ cm^{2}*	μ_{eff}** B.M.
	Mo	F	N		
$Mo_2O_3(dipy)_2F_4$	30.2 (30.5)	12.6 (12.1)	9.2 (8.9)	9	0.65
$Mo_2O_3(phen)_2F_4$	28.2 (28.4)	10.8 (11.2)	8.4 (8.2)	9	0.69
$Mo_2O_4(dipy)_2F_2$	31.2 (31.6)	6.0 (6.3)	9.1 (9.2)	8	0.28
$Mo_2O_4(phen)_2F_2$	29.1 (29.3)	5.7 (5.8)	8.4 (8.6)	5	0.15

* 10^{-3} *M* dimethyl sulphoxide solution except $Mo_2O_4(dipy)_2F_2$ (methanolic solution) at 25°.

** Per molybdenum atom at 27°.

TABLE 2—IR SPECTRAL BANDS (cm^{-1})

Compound	ν_{Mo-O_t}	$\nu_{MoO_2Mo/MoOMo}$	Other bands
$Mo_2O_3(dipy)_2F_4$	950 vs, 960 s	730 s	3420 m, 3110 w, 3075 w, 2920 vw, 2825 vw, 1595 s, 1570 vw, 1490 vw, 1470 m, 1440 vs, 1380 vw, 1315 m, 1160 vw, 1025 m, 930 m, 910 m, 790 s, 770 vs, 655 vw, 635 vw, 570 s, 550 s, 525 m, 505 s, 420 vw, 365 vw.
$Mo_2O_3(phen)_2F_4$	950 vs, 925 s	735 s, 725 vs	3420 m, 3050 w, 2920 vw, 1620 w, 1600 vw, 1575 w, 1515 m, 1490 vw, 1425 vs, 1380 vw, 1340 vw, 1220 vw, 1140 vw, 1105 vw, 895 w, 870 m, 850 vs, 780 m, 650 w, 570 m, 555 w, 500 m, 485 w, 425 w, 370 vw.
$Mo_2O_4(dipy)_2F_2$	950 vs	735 vs	3410 s, 3050 m, 1590 m, 1460 m, 1430 s, 1308 m, 1275 w, 1240 w, 1220 w, 1155 m, 1100 w, 1055 w, 1025 m, 875 m, 800 m, 765 vs, 650 m, 635 m, 605 m, 490 m.
$Mo_2O_4(phen)_2F_2$	955 vs	730 s	3470 m, 3050 w, 1600 w, 1575 w, 1510 w, 1490 w, 1420 m, 1335 w, 1300 w, 1220 w, 1140 w, 1105 w, 870 m, 850 s, 790 m, 640 m, 608 m, 500 m, 470 m, 420 w.

Results and Discussion

Both the complexes containing $Mo_2O_3^{4+}$ are deep violet in colour and are insoluble in water and other common organic solvents except having a low solubility in acetone and dimethyl sulphoxide. The complexes containing the moiety $Mo_2O_4^{2+}$ are reddish brown in colour. $Mo_2O_4(dipy)_2F_2$ is feebly soluble in water, methanol and ethanol, while $Mo_2O_4(phen)_2F_2$ is moderately soluble in dimethyl sulphoxide. The low molar conductances of $1.0\times 10^{-3}M$ solutions in dimethyl sulphoxide (methanol in the case $Mo_2O_4(dipy)_2F_2$) show the nonelectrolytic behaviour of the complexes (Table 1). As expected, all the complexes are very weakly paramagnetic, μ_{eff} varying from 0.15 to 0.69 B.M. (Table 1) at 27°.

The ir spectra of all the complexes (Table 2) show intense terminal ν_{Mo-O_t} stretches around 950 cm^{-1}. There is no ligand absorption in this range. Strong absorptions around 730 cm^{-1} may be safely assigned to bridging MoO_2Mo or MoOMo vibrations, since 1,10-phenanthroline does not absorb strongly in this region. 2,2′-Dipyridyl gives a strong band[8] at 755 cm^{-1}, which is observed as a separate band at 765 and 770 cm^{-1} in the spectra of both the complexes containing this ligand. The assignment of a second band characteristic of a MoO_2Mo or MoOMo group[9] in the lower frequency region is difficult because of the occurrence of Mo-F bands in this region.

The electronic spectra of the complexes containing the $Mo_2O_4^{2+}$ moiety give bands in the regions of about 32000 and 22000 cm^{-1} (Table 3). The complexes containing the $Mo_2O_3^{4+}$ unit, however, show strong absorption bands (in addition to those given by the complexes containing $Mo_2O_4^{2+}$ unit) in the lower region, *i.e.* 17000 and 13000 cm^{-1}. These spectral characteristics are quite in accordance with other similar complexes[10] of molybdenum.

TABLE 3—ELECTRONIC SPECTRA OF COMPLEXES

Compounds	ν, cm^{-1}
$Mo_2O_3(dipy)_2F_4$	34500 m, 23200 vs, 16600 vs, 13300 vs
$Mo_2O_3(phen)_2F_4$	32200 m, 23500 vs, 17200 vs, 13200 m
$Mo_2O_4(dipy)_2F_2$	33300, 22000
$Mo_2O_4(phen)_2F_2$	32200, 22000

The thermogram of the complexes showed that they begin to decompose very slowly from about 60° and the decomposition is very rapid from about 240° and finally at 470-550° they form MoO_3.

References

1. M. C. CHAKRAVORTI and A. K. BERA, *Transition Met. Chem.*, 1983, **8**, 83.
2. R. MATTES and G. LUX, *Angew. Chem.*, 1974, **86**, 598.
3. R. MATTES, K. MENNEMANN, H. RIESKAMP and H. BROCKMEYER, *J. Less-Common Met.*, 1980, **76**, 199.
4. R. KERGOAT and J. E. GUERCHAIS, *Bull. Soc. Chim. Fr.*, 1972, 1746.
5. W. G. PALMER, "Experimental Inorganic Chemistry", University Press, Cambridge, 1954, p. 406.
6. M. C. CHAKRAVORTI and S. C. PANDIT, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3644.
7. J. LEWIS and R. G. WILKINS, "Modern Coordination Chemistry", Interscience Publishers, New York, 1960, p. 403.
8. R. J. H. CLARK, *J. Chem. Soc.*, 1963, 1377.
9. E. I. STIEFEL, *Prog. Inorg. Chem.*, 1977, **22**, 85.
10. E. I. STIEFEL, *Prog. Inorg. Chem.*, 1977, **22**, 77.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 838-841

Lanthanide Iodide and Perchlorate Complexes of 4-*N*-(2′-Hydroxybenzylidine)aminoantipyrine

P. K. RADHAKRISHNAN

Department of Chemistry, University College, Trivandrum-695 034

Manuscript received 15 February 1984, accepted 20 September 1984

Eighteen new complexes of lanthanide iodides and perchlorates with 4-*N*-(2′-hydroxybenzylidene)aminoantipyrine (HBAAP) have been prepared and characterized. They have the general formulae, $[Ln(HBAAP)_6I]I_2$, where Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y, and $[Ln(HBAAP)_n](ClO_4)_3$, where n = 4 for La, Pr and Nd, and n = 5 for Sm, Gd, Tb, Dy, Ho and Y. Conductance studies indicate 1 : 2 electrolytic behaviour for the iodide complexes and 1 : 3 electrolytic behaviour for the perchlorate complexes. The magnetic moments of all the complexes agree well with Van Vleck values. Their infrared spectra reveal that HBAAP acts as a bidentate neutral ligand, one of the iodides is coordinated and none of the perchlorates is coordinated. Electronic spectra of the Nd complexes show weak covalency in the lanthanide-ligand bond. Thermogravimetric studies of the complexes indicate that these complexes are stable upto 200° and undergo complete decomposition in the range 200-620° forming the respective stable lanthanide oxides.

IN the earlier communication[1], we have reported on the preparation and characterisation of the complexes of 4-*N*-(2′-hydroxybenzylidene)aminoantipyrine (HBAAP) with lanthanide nitrates. In this communication we report on our studies of the complexes of HBAAP with lanthanide iodides and perchlorates. The iodide complexes are very interesting that one of the iodide ions is coordinated to the metal ion.

Experimental

Reagents: The iodides or perchlorates of La, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y were prepared by dissolving the respective oxides (99.9% pure) in 50% hydroiodic acid or perchloric acid and crystallising the salts on evaporation of the solution on a water bath. HBAAP was prepared from 4-aminoantipyrine and 2-hydroxybenzaldehyde by the method reported earlier[1,2].

Preparation and analysis of complexes: The lanthanide iodide complexes were prepared as follows. Lanthanide iodide (2 mmol) and HBAAP (12 mmol) in hot methanol were mixed and the resulting solution was kept under reflux for 1 h. The black viscous mass obtained on concentration of the solution was washed several times with hot benzene to remove the excess ligand. The solid complex separated was recrystallised by dissolving it in the minimum amount of methanol and stirring vigourously with the addition of diethyl ether. The complex separated was dried in vacuum over P_4O_{10}. The perchlorate complexes were prepared by the same method as in the case of the iodide complexes except that acetone was used as the solvent instead of methanol. All these complexes were analysed for metal, iodide and perchlorate by the conventional methods[3-5].

Physical methods: The physical methods used in the present investigation were the same as described earlier[1]. The far- infrared spectra were recorded on a Fourier far- ir spectrophotometer using KBr disc technique.

Results and Discussion

Analytical data (Table 1) of the complexes show that the iodide complexes have the general formula $Ln(HBAAP)_6I_3$, where Ln=La, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y, and the perchlorate complexes have the formula $Ln(HBAAP)_n(ClO_4)_3$, where n=4 for Ln=La, Pr and Nd, and n=5 for Ln=Sm, Gd, Tb, Dy, Ho and Y. All these complexes are mushroom coloured non-hygroscopic solids soluble in polar solvents, like acetone, acetonitrile, methanol and ethanol and insoluble in solvents of low polarity, like benzene, carbon tetrachloride and chloroform.

The molar conductance values (Table 1) of the iodide complexes in nitrobenzene show 1 : 2 eletrolytic behaviour[6,7]. The iodide complexes dissociate slightly in acetonitrile giving values slightly higher than those expected for 1 : 2 electrolytes[6,7]. But in the more polar solvent methanol they show 1 : 3 electrolytic behaviour[6,7], which is due to displacement of the coordinated iodide by methanol molecule[6]. The perchlorate complexes show 1 : 3 electrolytic behaviour in all of these solvents[7,8]. Thus, the iodide and perchlorate complexes may be formulated as $[Ln(HBAAP)_6I]I_2$ and [Ln-

TABLE 1—ANALYTICAL, CONDUCTANCE AND MAGNETIC DATA OF LANTHANIDE IODIDE AND PERCHLORATE COMPLEXES OF HBAAP

Sl. no.	Compound	Analysis % : Found/(Calcd.) Metal	Anion	Molar conductance* $C_6H_5NO_2$	CH_3CN	CH_3OH	μ_{eff} B.M.
1.	$[La(HBAAP)_5I]I_2$	6.84 (6.76)	18.41 (18.53)	38.58	320.8	245.0	–
2.	$[Pr(HBAAP)_5I]I_2$	6.97 (6.85)	18.86 (18.51)	42.00	324.7	249.2	3.51
3.	$[Nd(HBAAP)_5I]I_2$	7.06 (7.01)	18.04 (18.48)	40.64	318.3	242.3	3.64
4.	$[Sm(HBAAP)_5I]I_2$	7.19 (7.28)	18.56 (18.43)	39.05	318.9	250.4	1.66
5.	$[Gd(HBAAP)_5I]I_2$	7.58 (7.59)	18.51 (18.37)	40.35	322.9	257.8	7.81
6.	$[Tb(HBAAP)_5I]I_2$	7.40 (7.66)	18.13 (18.35)	43.56	317.8	247.2	9.65
7.	$[Dy(HBAAP)_5I]I_2$	7.92 (7.82)	18.51 (18.32)	41.32	322.7	242.4	10.61
8.	$[Ho(HBAAP)_5I]I_2$	7.79 (7.93)	18.27 (18.30)	40.35	321.3	240.8	10.25
9.	$[Y(HBAAP)_5I]I_2$	4.39 (4.44)	19.15 (18.99)	41.76	319.4	247.3	–
10.	$[La(HBAAP)_4](ClO_4)_3$	8.18 (8.34)	17.03 (17.92)	62.03	400.9	251.6	–
11.	$[Pr(HBAAP)_4](ClO_4)_3$	8.42 (8.45)	17.58 (17.90)	62.85	436.5	249.6	3.59
12.	$[Nd(HBAAP)_4](ClO_4)_3$	8.68 (8.64)	17.96 (17.86)	61.36	390.1	255.3	3.49
13.	$[Sm(HBAAP)_5](ClO_4)_3$	7.60 (7.58)	14.81 (15.04)	70.46	434.7	252.7	1.56
14.	$[Gd(HBAAP)_5](ClO_4)_3$	8.09 (7.90)	14.60 (14.99)	68.72	435.3	254.6	7.82
15.	$[Tb(HBAAP)_5](ClO_4)_3$	7.91 (7.98)	14.96 (14.98)	69.79	401.8	257.5	9.66
16.	$[Dy(HBAAP)_5](ClO_4)_3$	8.02 (8.14)	14.97 (14.95)	63.28	432.7	256.8	10.23
17.	$[Ho(HBAAP)_5](ClO_4)_3$	8.03 (8.25)	14.77 (14.93)	64.51	413.5	253.4	10.58
18.	$[Y(HBAAP)_5](ClO_4)_3$	4.53 (4.63)	15.54 (15.52)	63.50	414.9	251.4	–

* In ~ 10^{-3} M solution, Ω^{-1} cm^2 mol^{-1}.

$(HBAAP)_{4/5}](ClO_4)_3$, respectively. The observed magnetic moments of all these iodide and perchlorate complexes agree well with the Van Vleck values[9], which suggests that the 4f electrons in these complexes do not participate in bond formation.

The important infrared spectral bands of the complexes are presented in Table 2. The broad medium band around 3440 cm^{-1} attributed to the OH stretching vibration of the phenolic group[10] of HBAAP does not undergo appreciable shift in all of these complexes. The phenolic C-O stretching band[11] at 1310 cm^{-1} in HBAAP is also not shifted appreciably in the spectra of the complexes. Thus, the phenolic oxygen is not coordinated to the lanthanide ion. The very strong carbonyl stretching band at 1655 cm^{-1} in HBAAP is shifted to lower frequency by ~ 50 cm^{-1} in these complexes, indicating that the carbonyl oxygen is coordinated[8]. The strong band at 1590 cm^{-1} in HBAAP due to hydrogen-bonded C=N stretching vibration[12] is shifted to lower frequency by ~ 20 cm^{-1}. This indicates coordination of azomethine nitrogen to the central lanthanide ion with consequent decrease in carbon-nitrogen bond order[13-15]. Thus, HBAAP acts as a bidentate neutral ligand in all these complexes, coordinating through the carbonyl oxygen and azomethine nitrogen forming a five-membered ring.

The far- infrared spectra of the iodide complexes show a strong band around 160 cm^{-1} which is not present in the spectrum of the free ligand. This band is assigned to the metal-iodide stretching vibration[16-18]. This result confirms the coordination of one of the iodide ions to the metal ion. The appearance of two unsplit bands in the infrared spectra of the perchlorate complexes, a strong one at ~ 1085 cm^{-1} (ν_3) and a medium one at ~ 620 cm^{-1} (ν_4) indicates that the perchlorate group is not coordinated in these complexes[19].

The electronic spectra of these complexes in acetonitrile show a very broad band in the visible region with absorption maximum around 17.54 kK which may be assigned to the very strong ligand to metal charge transfer transition. Most of the bands due to f-f transition of the lanthanide ions could not be located in the visible region in the present complexes. This is due to the fact that the f-f bands are very weak and that they are masked by the very broad charge transfer band that spreads over the whole visible region[20].

TABLE 2—IMPORTANT IR BANDS (cm^{-1}) AND THERMAL DECOMPOSITION DATA OF LANTHANIDE IODIDE AND PERCHLORATE COMPLEXES OF HBAAP

Sl. no.	Compound	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_3(ClO_4)$	ν_{Ln-I} or $\nu_4(ClO_4)$	Decomp. temp. from TG °C
1.	$[La(HBAAP)_6I]I_2$	1605 vs	1575 vs		161 s	200
2.	$[Pr(HBAAP)_6I]I_2$	1605 vs	1570 vs		160 s	220
3.	$[Nd(HBAAP)_6I]I_2$	1605 vs	1570 vs		162 s	200
4.	$[Sm(HBAAP)_6I]I_2$	1605 vs	1570 vs		159 s	200
5.	$[Gd(HBAAP)_6I]I_2$	1600 vs	1570 vs		160 s	200
6.	$[Tb(HBAAP)_6I]I_2$	1610 vs	1570 vs		163 s	200
7.	$[Dy(HBAAP)_6I]I_2$	1610 vs	1565 vs		160 s	240
8.	$[Ho(HBAAP)_6I]I_2$	1605 vs	1570 vs		160 s	220
9.	$[Y(HBAAP)_6I]I_2$	1610 vs	1570 vs		160 s	240
10.	$[La(HBAAP)_4](ClO_4)_3$	1605 vs	1575 vs	1085 vs	620 m	220
11.	$[Pr(HBAAP)_4](ClO_4)_3$	1605 vs	1570 vs	1085 vs	620 m	200
12.	$[Nd(HBAAP)_4](ClO_4)_3$	1605 vs	1570 vs	1090 vs	620 m	200
13.	$[Sm(HBAAP)_6](ClO_4)_3$	1605 vs	1565 vs	1085 vs	620 m	200
14.	$[Gd(HBAAP)_6](ClO_4)_3$	1600 vs	1570 vs	1080 vs	620 m	200
15.	$[Tb(HBAAP)_6](ClO_4)_3$	1605 vs	1575 vs	1090 vs	620 m	220
16.	$[Dy(HBAAP)_6](ClO_4)_3$	1605 vs	1575 vs	1090 vs	620 m	200
17.	$[Ho(HBAAP)_6](ClO_4)_3$	1600 vs	1575 vs	1090 vs	620 m	220
18.	$[Y(HBAAP)_6](ClO_4)_3$	1600 vs	1575 vs	1090 vs	620 m	200

m = medium; vs = very strong; s = strong.

However, in the Nd iodide and perchlorate complexes, the following f-f bands are observed, the tentative assignments of which are given in brackets.

Nd iodide complex:

19.08 kK($^4I_{9/2}\rightarrow{}^4G_{7/2}$); 17.24 kK($^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^2G_{7/2}$); 13.44 kK($^4I_{9/2}\rightarrow{}^4F_{7/2}$); and 12.48 kK ($^4I_{9/2}\rightarrow{}^2H_{9/2}$).

Nd perchlorate complex:

19.08 kK($^4I_{9/2}\rightarrow{}^4G_{7/2}$); 17.21 kK($^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^2G_{7/2}$); 13.42 kK($^4I_{9/2}\rightarrow{}^4F_{7/2}$); and 12.50 kK ($^4I_{9/2}\rightarrow{}^2H_{9/2}$).

A small red-shift is observed in these f-f bands compared to the aquo ion[21,22]. Sinha covalency parameters[21] calculated for these two Nd complexes (δ=0.7049 for the iodide complex and δ=0.7354 for the perchlorate complex) show weak covalency in the lanthanide-ligand bond.

Thermogravimetric data (Table 2) of the complexes show that all the complexes are stable upto ~ 200°. All the iodide complexes undergo decomposition in two stages as denoted by the two well-defined DTG peaks around 250-325° and 430-450°. All the perchlorate complexes undergo decomposition in three stages as represented by the DTG peaks around 270-325°, 390-430° and 470-495°. The decomposition of all the iodide and perchlorate complexes is complete in the range 480-620° leaving behind the respective stable lanthanide oxides.

Acknowledgement

The author would like to thank Prof. C. G. R. Nair, Dr. C. P. Prabhakaran, and Dr. P. Indrasenan for some helpful discussion and to Prof. C. P. Joshua for providing facilities in the Department of Chemistry, University of Kerala.

References

1. P. K. RADHAKRISHNAN, P. INDRASENAN and C. G. R. NAIR, *Polyhedron*, 1984, 3, 67.
2. T. RADHAKRISHNAN, P. T. JOSEPH and C. P. PRABHAKARAN, *J. Inorg. Nucl. Chem.*, 1976, 38, 2217.
3. I. M. KOLTHOFF and P. J. ELVING, "Treatise on Analytical Chemistry", Interscience, New York, 1963, Vol. 8, p. 34.
4. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", E. L. B. S., London, 1961, p. 343.
5. E. KURZ, G. KOBER and M. BERL, *Anal. Chem.*, 1958, 30, 1983.

6. W. J. GEARY, *Coord. Chem. Rev.*, 1971, **7**, 81.
7. G. B. DEACON, J. H. S. GREEN and R. S. NYHOLM, *J. Chem. Soc.*, 1965, 3411.
8. C. G. R. NAIR and P. K. RADHAKRISHNAN, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1981, **90**, 541.
9. J. H. VAN VLECK and N. FRANK, *Phys. Rev.*, 1929, **34**, 1494.
10. L. J. BELLAMY, "Infrared Spectra of Complex Molecules", Chapman and Hall, London, 1954, p. 108.
11. J. E. KOVACIC, *Spectrochim. Acta, Part A*, 1967, **23**, 183.
12. K. UENO and A. E. MARTELL, *J. Phys. Chem.*, 1956, **60**, 1270.
13. B. D. SARMA and J. C. BAILAR, Jr., *J. Am. Chem. Soc.*, 1955, **77**, 5476.
14. P. GLUVCHINSKY, G. M. MOCKLER and E. SINN, *Spectrochim. Acta, Part A*, 1977, **33**, 1073.
15. A. SYAMAL, *Transition Met. Chem.*, 1980, **5**, 220.
16. K. NAKAMATO, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, 1970, p. 214.
17. D. M. ADAMS and P. J. CHANDLER, *Chem. Comm.*, 1966, **3**, 69.
18. D. M. ADAMS, P. J. CHANDLER and R. G. CHURCHILL, *J. Chem. Soc. (A)*, 1967, 1274.
19. B. J. HATHAWAY and A. E. UNDERHILL, *J. Chem. Soc.*, 1961, 3091.
20. M. V. KRISHNAMURTHY, I. M. RAO and D. SATHYANARAYANA, *Indian J. Chem., Sect. A*, 1982, **21**, 827.
21. S. P. SINHA, *J. Inorg. Nucl. Chem.*, 1965, **27**, 115.
22. S. P. SINHA, *Spectrochim. Acta*, 1966, **22**, 57.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 842-846

A Quantitative Approach to Stability Correlations of Some Lanthanide-Edta-Hydroxy Acid Ternary Complexes

S. N. LIMAYE and M. C. SAXENA*

Department of Chemistry, Dr. Harisingh Gour Vishwavidyalaya, Sagar-470 003

Manuscript received 16 March 1984, accepted 15 August 1984

Metal-ligand stability constants of the mixed-ligand complexes of lanthanide metal ions, viz. La^{III}, Ce^{III}, Pr^{III}, Nd^{III} and Sm^{III} with edta as primary ligand and malic (ma), lactic (la), glycolic (ga), or gluconic (gluc) acid as secondary ligand have been determined *p*H-metrically at 25° and ionic strength of 0.2 (mol dm^{-3} $NaClO_4$), using Irving-Rossotti titration technique. The ternary systems are of the type, $M + A \rightleftharpoons MA$, $MA + L \rightleftharpoons MAL$. The log K^{MA}_{MAL} values have been found to lie in the sequence $La^{III} < Ce^{III} < Pr^{III} < Nd^{III} < Sm^{III}$ with respect to metal ions, and ma > la > ga > gluc with respect to the secondary ligands. The Δlog K values are negative due to electrostatic effects. Six log-log type stability correlations have been discussed with the help of mathematical equations derived for the purpose. It has been found that the plots of (i) log K^{M}_{ML} *vs* log K^{H}_{HL}, (ii) log K^{MA}_{MAL}, *vs* log K^{H}_{HL}, (iii) log K^{MA}_{MAL} *vs* log K^{M}_{MA}, (iv) log K^{MA}_{MAL} *vs* log K^{M}_{ML}, (v) log K^{MA}_{MAL} *vs* log $K^{MA}_{MAL''}$, and (vi) log K^{MA}_{MAL} *vs* log $K^{M'A}_{M'AL}$, are all linear with non-unit slopes.

CORRELATIONS between the stability constants of binary metallic complexes and the properties of metal ions and ligands have been discussed at length[1-4]. A linear relationship exists[5,6] between the basicity of secondary ligands and the stability constants of mixed-ligand complexes of the type (M-dipy-L). Some aspects of structure and stability of ternary complexes have recently been reviewed[7]. Correlations between the stability constants of ternary lanthanide complexes with some fundamental properties of the metal ions and ligand characteristics have been reported by us[8].

The present communication deals with a quantitative study of some log-log type correlations amongst the stability constants of the mixed complexes of La^{III}, Ce^{III}, Pr^{III}, Nd^{III} and Sm^{III} (LN=lanthanide) using edta as primary ligand and aliphatic hydroxy acids, malic (ma), lactic (la), glycolic (ga), or gluconic (gluc) as secondary ligands.

Experimental

Standard solutions of metal ions and edta were prepared as reported earlier by us[8].

The solutions of ma, la, ga and gluc were prepared in double-distilled water. The formation constants of the mixed complexes have been determined by using Irving-Rossotti *p*H-titration technique[9] and its extension to ternary systems[10]. Usual titration sets for 1 : 1 binary and 1 : 1 : 1 ternary complexes were prepared keeping the ionic strength constant at 0.2 (mol dm^{-3} $NaClO_4$) and titrated against 0.2 mol dm^{-3} carbonate-free sodium hydroxide at 25°. The *p*H values of the solutions were recorded on an Elico LI-120 digital *p*H meter. A representative set of plots of *p*H *vs* ml of alkali for (La-edta-ma) system has beenshown in Fig. 1.

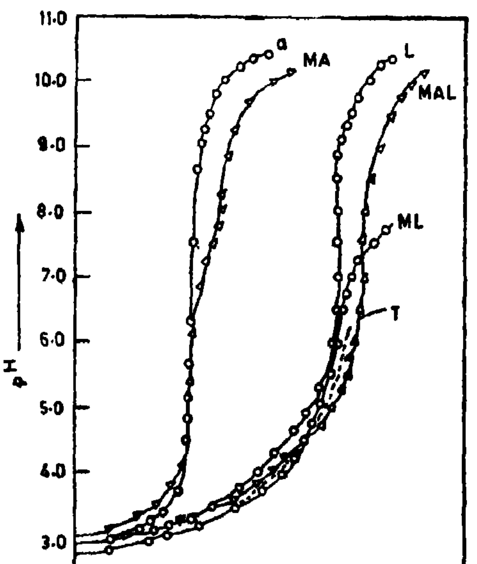


Fig. 1. Representative *p*H-tiration plots for 1 : 1 binary and 1 : 1 : 1 ternary La^{3+}-edta-ma : Systems : a = acid, L = ma, MA = LN-edta, ML = LN-ma, MAL = La-edta-ma, T = composite curve.

Results and Discussion

The metal-ligand stability constants of the ternary complexes (log K^{MA}_{MAL}) along with other

TABLE 1—METAL-LIGAND STABILITY CONSTANTS OF 1 : 1 : 1 TERNARY COMPLEXES AND OTHER RELATED PROPERTIES

I = 0.2 (mol dm^{-3} $NaClO_4$) Temp. = 25°

Secondary ligand	Property	La^{III}	Ce^{III}	Pr^{III}	Nd^{III}	Sm^{III}
Malic acid (ma)	log K^{MA}_{MAL}	3.38	3.46	3.53	3.75	4.11
	−Δ log K	0.37	0.55	0.67	0.70	0.42
	−ΔG(kJ mol^{-1})	16.44	16.87	17.19	18.24	20.04
	log K_s	9.59	9.87	10.16	10.51	10.77
	−(%) R.S.	9.80	13.71	15.95	15.73	9.27
	(%) R.A.	64.75	64.90	65.25	64.31	61.83
Lactic acid (la)	log K^{MA}_{MAL}	3.35	3.43	3.55	3.68	3.86
	−Δ log K	0.33	0.31	0.43	0.31	0.26
	−ΔG (kJ mol^{-1})	16.31	16.69	17.30	17.99	18.82
	log K_s	9.57	9.81	10.11	10.40	10.67
	−(%) R.S.	8.96	8.29	10.80	7.77	6.31
	(%) R.A.	64.99	65.03	64.88	64.62	63.82
Glycolic acid (ga)	log K^{MA}_{MAL}	3.28	3.47	3.55	3.64	3.72
	−Δ log K	0.32	0.16	0.13	0.19	0.20
	−ΔG(kJ mol^{-1})	16.03	16.87	17.44	17.59	18.13
	log K_s	9.55	9.76	10.04	10.36	10.62
	−(%) R.S.	8.88	4.40	3.50	4.96	5.10
	(%) R.A.	65.65	64.44	64.3	64.86	64.97
Gluconic acid (gluc)	log K^{MA}_{MAL}	2.13	2.46	2.69	2.86	2.92
	−Δ log K	0.86	0.70	0.57	0.60	0.62
	−ΔG(kJ mol^{-1})	10.37	11.96	13.11	13.63	14.23
	log K_s	9.39	9.68	9.93	10.25	10.52
	−(%) R.S.	28.00	22.15	17.48	17.60	17.51
	(%) R.A.	77.31	74.58	72.19	72.09	72.24

related values, *viz*. ΔG ($\Delta G = -2.303\ RT \log K^{MA}_{MAL}$), Δlog K, log K_s, (%) R.S. and (%) R.A. (terms explained latter) of the ternary complexes have been recorded in Table 1.

The *p*H-titration plots in Fig. 1 indicate that the ternary systems under study are of the type $M + A \rightleftharpoons MA$, $MA + L \rightleftharpoons MAL$, where the secondary ligand L combines with MA (a stable primary complex whose *p*H of formation is much below the *p*H of formation of mixed complexes) to form a mixed complex MAL. The much stronger complexing tendency of edta eliminates the possibility of any ligand displacement of the type $MA + L \rightleftharpoons ML + A$. Also, the hexadentate nature of edta minimises the possibility of formation of species MA_2 or the disproportionation of MAL into MA_2 or ML_2[11]. The formation of mixed complexes has been confirmed by the non-superimposable nature of the theoretical composite curve[12] on the experimental mixed complex curve. The formation of mixed complexes takes place at the *p*H where the formation of hydroxo species can be ignored. The plots of $\bar{n}$/[L] *vs* [L] (Fig. not shown) have been found to be smooth, indicating the absence of any protonated or polynuclear species.

The general order of stability for the complexes has been found to be log K^{M}_{MA} >> log K^{M}_{ML} > log K^{MA}_{MAL}. The lower values of log K^{MA}_{MAL} than log K^{M}_{ML} may be due to coulombic repulsion between the negatively charged primary complex $(LN\text{-}edta)^-$ and the incoming secondary ligand L^- or L^{2-} during the formation of ternary complexes. The Δ log K values are consequently negative.

The Δ log K values measure the relative ease or difficulty in the formation of mixed-ligand complex MAL as compared to ML. The magnitude of Δ log K cannot, however, be compared for different mixed complexes as its value depends on the log K^{M}_{ML} value. A parameter '% Relative Stabilisation' (R.S.) for the ternary complex may be defined as,

$$(\%)\ R.S. = [(\log K^{MA}_{MAL} - \log K^{M}_{ML})/\log K^{M}_{ML}] \times 100.$$

The values of (%) R.S. may be compared for the mixed-ligand complexes to estimate their relative stabilisation at a certain temperature. In the present case the numerical values of ( ) R.S. lie in the range 9.27-15.95 for ma, 6.31-10.80 for la, 3.50-8.88 for ga and 17.48-28.0 for gluc. It seems that, as pointed out by Grenthe[13] for binary complexes of la and ga on the basis of thermodynamic parameters, the bonding between lanthanide metal ion and hydroxyl group takes place *via* a water molecule through hydrogen bonding rather than a direct LN-O bond being formed with the hydroxyl group.

The values of statistical stability constant[14] (log K_s) have also been calculated for the present set of complexes, assuming lanthanide metal ion as octacoordinate, edta as hexadentate and secondary ligand as bidentate. The calculated log K_s values are found to be greater than log K^{MA}_{MAL} values which explains the involvement of astatistical factors

(mainly electrostatic) during the formation of mixed complexes.

Another new parameter '(%) Relative Astatisticality' (R.A.) of the ternary complex may be defined as,

$$(\%)\ \text{R.A.} = [\log K_s - \log K^{MA}_{MAL})/\log K_s] \times 100.$$

The numerical values of (%) R.A. may be used for a quantitative estimation of the relative astatisticality involved in the formation of the ternary complexes at a certain temperature. The values of (%) R.A. in the present case are found to vary between 61 to 65% for ma, la and ga, and about 72 to 77% for gluc mixed complexes.

The sequence of log K^{MA}_{MAL} values with respect to the secondary ligands has been found to be ma>la>ga>gluc, which is the order of their basicity. Similar results are reported in for the (LN-cdta.L) chelates[15] (where, LN=La^{III}, Pr^{III} Nd^{III}, L=ma, la, ga). The lower values of stability for the gluc ternary systems may be due to greater steric repulsion involved in its case Of the secondary ligands in the present case, ga and la are closely related. Substitution of additional methyl group in la should cause a lowering in the stability of the resulting ternary complexes, but the observed sequence is reverse, *i.e.* la>ga, which is in good agreement with the values of similar ternary complexes reported[16,17]. This may be due to a cooperative effect between the primary and secondary ligands (la) in the ternary systems.

The stability sequence with respect to metal ions has been found to be $La^{III} < Ce^{III} < Pr^{III} < Nd^{III} < Sm^{III}$, which is the order of increasing ionic potentials of these metal ions. It is interesting to note that the metal ions under study have almost identical electronegativities. On going from La^{III} to Sm^{III} the ionic radii, the sum of the first three ionisation potentials and their polarising powers vary by 7.5% (decrease), 11.6% (increase) and 16.6% (increase), respectively. The increase in log K^{MA}_{MAL} values is about 21% for ma, 15% for la, 13% for ga, and as much as 37% for gluc. It is evident that apart from the above metal characteristics, these ligands cause varying degrees of stabilisation in the ternary systems.

Stability correlations (log-log type): Some log-log type stability correlations have been discussed adopting a mathematical approach. The expressions correlating the two stability constants have been derived by combining the relationships involving free energy changes during the formations of HL, ML and MAL and the relationships of the type, $\Delta G = -2.303$ RT log K. Equations (1) and (2) have been derived at standard conditions.

$$\log K^M_{ML} = \log K^H_{HL} + (2.303\ RT)^{-1}.[(G^0_M - G^0_H) + (G^0_{HL} - G^0_{ML})] \quad (1)$$

$$\log K^{MA}_{MAL} = \log K^H_{HL} + (2.303\ RT)^{-1}.[(G^0_{MA} - G^0_H) + (G^0_{HL} - G^0_{MAL})] \quad (2)$$

It is obvious from equations (1) and (2) that a plot of log K^M_{ML} *vs* log K^H_{HL} or log K^{MA}_{MAL} *vs* log K^H_{HL} will be linear if the first term within brackets on the right hand side is constant, and the second term is either negligible in comparison to the first term, or a constant, or a linear function of log K^H_{HL}. The first two conditions will lead to a plot of unit slope, the third to a non-unit slope. For a given metal ion the quantity $(G^0_M - G^0_H)$ in equation (1) and for a given primary complex the quantity $(G^0_{MA} - G^0_H)$ in equation (2) will be constant. The log-log plots, log K^M_{ML} *vs* log K^H_{HL}, and log K^{MA}_{MAL} *vs* log K^H_{HL} for the various systems under study are shown in Figs. 2(a) and

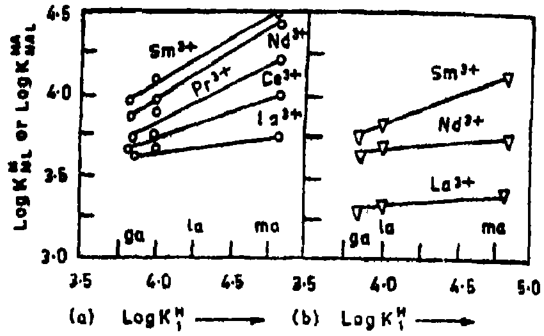


Fig. 2. Log-Log plots of (a) Log K^M_{ML} *vs* Log K^H_1 (o) and (b). Log K^{MA}_{MAL} *vs* Log K^H_1.

2(b) respectively. The slope values (Table 2) are all non-unity in both the cases showing the existence of the third possibility in these systems.

Four more equations (3) to (6) have also been derived.

$$\log K^{MA}_{MAL} = \log K^M_{MA} + (2.303\ RT)^{-1}.[(G^0_L - G^0_A) - (G^0_M - 2G^0_{MA} + G^0_{MAL})] \quad (3)$$

$$\log K^{MA}_{MAL} = \log K^M_{ML} + (2.303RT)^{-1}.[(G^0_{MA} - G^0_M) + [(G^0_{ML} - G^0_{MAL})] \quad (4)$$

$$\log K^{MA}_{MAL} = \log K^{MA}_{MAL'} + (2.303RT)^{-1}.[(G^0_L - G^0_{L'}) - (G^0_{MAL} - G^0_{MAL'})] \quad (5)$$

$$\log K^{MA}_{MAL} = \log K^{M'A}_{M'AL} + (2.303RT)^{-1}.[(G^0_{MA} - G^0_{M'A}) - (G^0_{MAL} - G^0_{M'AL})] \quad (6)$$

The first term in equations (3), (4) and (5) will be constant for a given set of ligands (permitting variation of metal ion), metal and primary ligand (permitting variation of secondary ligand), and closely related secondary ligands (permitting variation of metal ions for the same pair of secondary ligands), respectively.

The plots corresponding to equations (3), (4) and (5) have been shown in Figs. 3a, 3b and 3c, respectively. They are all linear. The slope values are given in Table 2. This again indicates that the second term within brackets on the right hand side in each case is a linear function of the corresponding first term on the right hand side as the slope values are non-unity. The literature values of log K^{MA}_{MAL} for the systems of the type (LN-cdta-L)[15] have been used with our log K^M_{ML} values under comparable

TABLE 2—SLOPE VALUES FOR LINEAR PLOTS REPRESENTING LOG-LOG TYPE CORRELATIONS

Correlation*	Slope values La^{III}	Ce^{III}	Pr^{III}	Nd^{III}	Sm^{III}
$\log K^{M}_{ML}$ *vs* $\log K^{H}_{HL}$ (eq. 1)	0.15	0.38	0.49	0.62	0.61
$\log K^{MA}_{MAL}$ *vs* $\log K^{H}_{HL}$ (eq. 2)	0.40	–	0.40	0.11	0.39
		ma	la	ga	gluc
$\log K^{MA}_{MAL}$ *vs* $\log K^{M}_{MA}$ (eq. 3)		0.55	0.39	0.33	0.56
$\log K^{MA}_{MAL}$ *vs* $\log K^{M}_{ML}$ (eq. 4) EDTA		0.93	1.15	1.32	1.36
$\log K^{MA}_{MAL}$ *vs* $\log K^{M}_{ML}$ (eq. 4) CDTA		1.18	1.93	0.93**	
$\log K^{MA}_{MAL}$ *vs* $\log K^{M'A}_{M'AL}$ (eq. 6)		1.75	1.30	0.69	0.68
$\log K^{MA}_{MAL}$ *vs* $\log K^{MA}_{MAL'}$ (eq. 5)			0.86		

* L = la, L′ = ga, ** Ref. 15.

conditions, for studying the log-log correlation represented by equation (4). The plots are linear (Fig. 3c). The slope values are mentioned in the Table 2 for comparison.

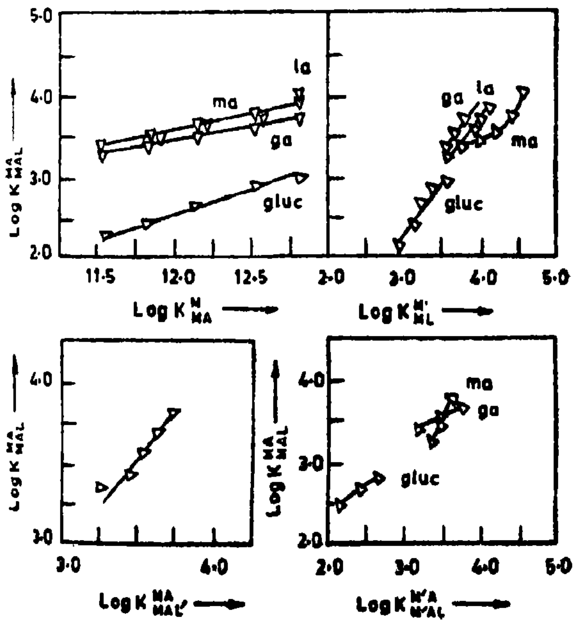


Fig. 3. Log-Log plots for (a) Log K^{MA}_{MAL} *vs* Log K^{M}_{MA}, (b). Log K^{MA}_{MAL} *vs* Log K^{M}_{ML}, (c). Log K^{MA}_{MAL} *vs* Log $K^{MA}_{MAL'}$, (L = la, L′ = ga), (d). Log K^{MA}_{MAL} *vs* Log $K^{M'A}_{M'AL}$.

In equation (6), however, the first term within brackets on the right hand side, *i.e.* $(G^{o}_{MA} - G^{o}_{M'A})$ may vary with metal ions. The plots log K^{MA}_{MAL} *vs* log $K^{M'A}_{M'AL}$ (Fig. 3d) are linear indicating that for the present set of metal ions this term remains rather constant.

Table 2 shows the slope values obtained for various log-log type correlations of the present study.

The deviations from linearity may be ascribed to considerations of enthalpy and/or entropy[18]. It is reported for some binary complexes that the slope values for the correlations between log K^{M}_{ML} and log K^{H}_{HL} (or log $\beta^{H}_{H_nL}$) depend on (i) ionisation potentials of the metal ions[19], (ii) nuclear repulsions between the metal ion and donor atom[20], or (iii) the polarisation of the ligand by metal ions[21]. A large number of suitably planned ternary systems will have to be studied before any generalisation may be possible.

Acknowledgement

The authors are thankful to Dr. Y. G. Kher, Head, Department of Chemistry for providing facilities. Thanks are also due to the M.P. Council of Science and Technology, Bhopal for a research grant (M.C.S.) and to the U.G.C., New Delhi for the award of a Senior Research Fellowship (S.N.L.).

References

1. F. J. C. ROSSOTTI in "Modern Coordination Chemistry", eds. J. LEWIS and R. G. WILKINS, Interscience Publishers, New York, 1960, pp. 39-63.
2. M. M. JONES, "Elementary Coordination Chemistry", Prentice-Hall, Englewood Cliffs, 1964, pp. 339-341.
3. S. CHABEREK and A. E. MARTELL, "Organic Sequestering Agents", John-Wiley, New York, 1959, pp. 125-173.
4. M. T. BECK, "Chemistry of Complex Equilibria", Van Nostrand Reinhold, London, 1970, pp. 240-265.
5. R. GREISSER, B. PRIJS and H. SIGEL, *Inorg. Nucl. Chem. Lett.*, 1968, 4, 443.
6. H. SIGEL, *J. Inorg. Nucl. Chem.*, 1975, 37, 507.
7. P. K. BHATTACHARYA, *J. Sci. Ind. Res.*, 1981, 40, 382.

8. S. N. LIMAYE and M. C. SAXENA, *J. Indian Chem. Soc.*, 1981, **59**, 698, 916.
9. H. M. IRVING and H. S. ROSSOTTI, *J Chem. Soc.*, 1953, 3397 ; 1954, 2904.
10. P. K. BHATTACHARYA and M. V. CHIDAMBARAM, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3271.
11. L. G. THOMPSON and J. A. LORAAS, *Inorg. Chem.*, 1963, **2**, 89.
12. G. H. CARREY and A. E. MARTELL, *J. Am. Chem. Soc.*, 1967, **89**, 2359.
13. I. GRENTHE, *Acta Chem. Scand.*, 1964, **18**, 283.
14. R. DEWITT and J. I. WATTERS, *J. Am. Chem. Soc.*, 1954, **76**, 3810.
15. H. S. RANA and J. P. TANDON, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1391.
16. J. D. JOSHI, B. R. PANCHAL and P. K. BHATTACHARYA, *J. Indian Chem. Soc.*, 1973, **50**, 344.
17. J. D. JOSHI and P. K. BHATTACHARYA, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1685.
18. S. J. ASHCROFT and C. T. MORTIMER, "Thermochemistry of Transition Metal Complexes", Academic Press, London, 1970, p. 308.
19. G. SCHWARZENBACH, H. ACKERMANN and P. RUCKSTUHL, *Helv. Chim. Acta*, 1949, **32**, 1175.
20. L. G. VAN UITERT, W. C. FERNELIUS, AECD-NYO, 1952, 3372 ; *J. Am. Chem. Soc.*, 1954, **76**, 379.
21. J. G. JONES, J. B. POOLE, J. C. TOMKINSON and R. J. P. WILLIAMS, *J. Chem. Soc.*, 1958, 2001.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 847-849

Complexes of Rare Earths and Their Biocidal Properties

S. P. TRIPATHI*, R. KUMAR**, G. K. CHATURVEDI and R. C. SHARMA***

Chemical Laboratories, Agra College, Agra-282 002

Manuscript received 30 November 1983, accepted 10 August 1984

Mixed-ligand complexes of the type MAB (where M = La^{III}, Pr^{III}, Nd^{III}, Gd^{III} and Dy^{III}; A = TAR (tartaric acid)/MAL (malic acid); B = HQ (8-hydroxyquinoline) have been investigated potentiometrically. During the formation of above species ligand B coordinates to the initially formed 1 : 1, MA complexes in the second step. Ir spectra and elemental analyses of the isolated complexes have also been carried out in support of the potentiometric results. The resulting complexes and involved ligands have been studied to find out the percentage inhibition (at 200 ppm) on some selected fungi and bacteria.

A survey of the literature revealed that the formation of binary and ternary complexes of rare earths with TAR and MAL[1-4] and HQ[5,6] as one of the ligands have been extensively studied. The information about the role of metal complexes in biological systems, their concentration and their presence in different equilibrium is of immense importance. Gershon *et al.*[7-8] reported that the activity of metal chelate is considerably increased as compared to that of the free metal and the ligands alone on their complexation. Similar observations have also been noted on 8-HQ[9] and by Cu^{II} complexes[10] with hydroxy acids and heterocyclic compounds and also on rare earth complexes[11]. In continuation to our previous studies[12,13] it was, therefore, thought worthwhile to investigate some more ternary complexes of rare earths involving HQ and hydroxy acids potentiometrically.

Experimental

All the chemicals used were either of the AR, BDH or Fluka grade. The standard solutions of metal nitrates[14], KNO_3, KOH, and potassium hydrogen phthalate[14], hydroxy acids[15] and $HQ.H^+$[5] were prepared as described earlier.

Instrument and methods : *p*H-metric titrations were carried out with a Philips PR 9405M *p*H meter with a calomel and standard glass electrode assembly, standardised for *p*H 4 at $25 \pm 1°$. The ir spectra (KBr) were recorded on a Perkin-Elmer IR 4250 spectrophotometer.

Results and Discussion

Similar curves were obtained for all the mixed systems M^{III}-TAR/MAL-HQ (where M^{III} = La^{III} Pr^{III}, Nd^{III}, Gd^{III} and Dy^{III}. For the sake of brevity only the curves for the systems La^{III}-TAR/MAL-HQ have been discussed.

Curve b (Figs. 1 and 2) ascribes the titration of HQ mono-hydrochloride. A well defined inflection at m=1 indicates titration of loosely attached proton of the $HQ.H^+$. A single well defined inflection at m=2 on the curve c (Figs. 1 and 2) shows the simultaneous titration of both the carboxylic protons of the acids[15] (TAR and MAL), respectively.

Binary systems : Curve d (Figs. 1 and 2) represents the potentiometric titration of 1 : 1, La^{III}-HQ binary mixture. An almost overlapping nature of this curve to the curve b upto m ~ 1 probably indicates the titration of the ligand hydrochloride alone in acidic medium. The occurrence of a yellow solid at m > 1 and the appearance of a sharp inflection at m=2 attributes to the formation of 1 : 3, La^{III}-HQ complex[5] which is further supported by the appearance of one more inflection at m ~ 4 probably due to the precipitation of the remaining metal as metal hydroxide and the colour of the solid phase changing from yellow to whitish yellow.

Curve e (Figs. 1 and 2) depicts the titration of 1 : 1, La^{III}-TAR/MAL binary systems, respectively. The lowering in initial *p*H and an inflection at m = 2 may be correlated to the formation of 1 : 1, binary complexes in both the cases. One more inflection at m = 3 in case of La^{III}-MAL can be attributed to the deprotonation of the initially formed protonated species resulting in the formation of a neutral complex[16] as evidenced by the formation of a solid phase at m > 2. The other inflection at m ~ 3.5 in the system 1 : 1 La^{III}-TAR (Fig. 1) may, however, be ascribed to the disproportionation of the initially formed 1 : 1 complex into 1 : 2, La^{III}-TAR soluble species[17] with the simultaneous precipitation of the remaining metal as its hydroxide at higher *p*H.

Ternary systems : The initial superimposable nature of the curve f (Fig. 1) for 1 : 1 : 1, La^{III}-

**National Chemical Laboratory, Pune-411 008.
***Agra University, Agra-282 002.

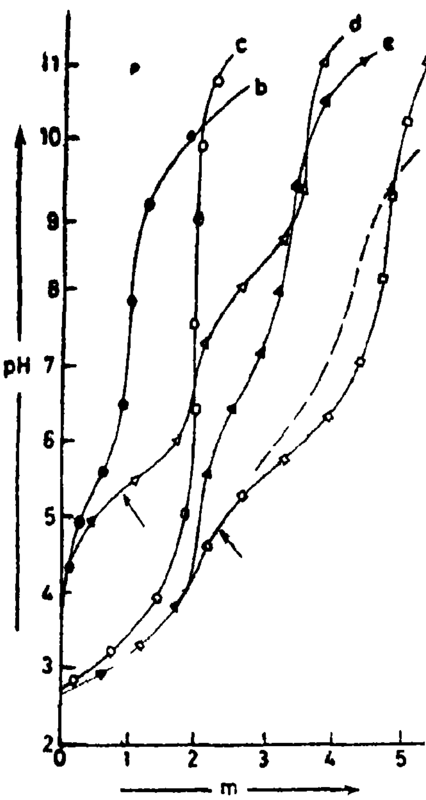


Fig. 1. Curve b = HQ.H$^+$; c = TAR ; d = 1 : 1, La^{III}-HQ ; e = 1 : 1, La^{III}-TAR ; f = 1 : 1 : 1, La^{III}-TAR-HQ ; T = Theoretical composite curve ; and → = appearance of ppt.

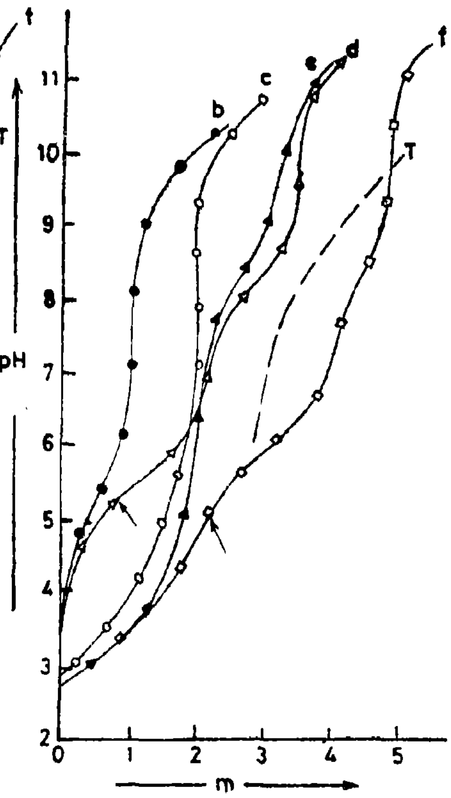


Fig. 2. Curve b = HQ.H$^+$; c = MAL ; d = 1 : 1, La^{III}-HQ ; e = 1 : 1, La^{III}-MAL ; f = 1 : 1 : 1, La^{III}-MAL-HQ ; T = Theoretical composite curve ; and → = appearance of ppt.

TAR-HQ mixed system to the curve e (Fig. 1) and an inflection at m=2 may be attributed to the formation of 1 : 1, La^{III}-TAR binary complex. The lowering in the upper buffer region, an appearance of a solid (at m>2) and its partial dissolution with a sharp inflection at m ~5 at higher *p*H (~8) may probably be attributed to the simultaneous coordination of the secondary ligand HQ and one of the OH groups of TAR to the initially formed 1 : 1, La^{III}-TAR binary complex resulting in the formation of 1 : 1 : 1, La^{III}-TAR-HQ ternary species as follows :

$$HQ.H^+ + [TAR-La^{3+}] + 3OH^- \underset{2<m<5}{\rightleftharpoons} [HQ^{1-}-La^{3+}-TAR^{3-}] + 3H_2O$$

The initial superimposable nature of the curve f to the curve e (Fig. 2) and an inflection at m=2 shows the priority of complexation of MAL with metal ion resulting in the formation of 1 : 1, La^{III}-MAL complex. The further lowering in *p*H and an inflection at m~4 may probably be correlated to the addition of HQ.H$^+$ to the initially formed 1 : 1, La^{III}-MAL complex. One more inflection at m ~5 can be ascribed to the titration of hydroxyl proton of the MAL at high *p*H as evidenced in the binary complex forming 1 : 1 : 1, soluble species as observed by an almost dissolution of the solid phase.

$$HQ.H^+ + [MAL^{2-}-La^{3+}] + 2OH^- \overset{2<m<4}{\rightleftharpoons} [HQ^{1-}-La^{3+}-MAL^{2-}] + 2H_2O$$

$$[HQ^{1-}-La^{3+}-MAL^{2-}] + OH^- \overset{4<m<5}{\longrightarrow} [HQ^{-1}-La^{3+}-MAL^{3-}] + H_2O$$

The formation of above ternary complexes is further supported by (i) non-superimposable nature of the theoretical composite curve T[18] with the curve f in the region of mixed ligand complex formation, (ii) a partial dissolution of solid phase at higher *p*H in both the cases, and (iii) ir spectral studies and the analyses of N, C, H and metal (M) of the isolated complexes (Table 1)

TABLE 1—ELEMENTAL ANALYSIS

Complex	Analysis : Found/(Calcd.)			
	M	N	C	H
La^{III}-HQ-TAR-H_2O	30.33 (30.85)	2.95 (3.11)	33.85 (34.65)	2.28 (2.44)
La^{III}-HQ-MAL-H_2O	30.78 (31.34)	3.05 (3.15)	34.00 (35.20)	2.40 (2.48)

Ir spectra : A comparative study of the ir spectra of the complexes with those of the involved ligands shows the appearance of some new bands as well as

TABLE 2—BIOCIDAL ACTIVITY

Fungi*/Bacteria**	Substance	Concn. ppm	Inhibition %
Aspergillus niger	HQ/TAR/MAL	200/500/500	88/20/25
Aspergillus flavus	HQ/TAR/MAL	200/500/500	90/10/10
Penicillium citrinum	HQ/TA/MAL	200/500/500	80/10/20
Aspergillus niger	La^{III}-TAR/MAL-HQ	200/200	100/100
Aspergillus flavus	La^{III}-TAR/MAL-HQ	200/200	100/100
Penicillium citrinum	La^{III}-TAR/MAL-HQ	200/200	100/100
Staphylococcus	La^{III}-TAR/MAL-HQ	200	78/90
Streptococcus	,,	200	90/100

* Antifunal activity at 28° after 96 h.
** Antibacterial activity after 48 h.

lowering in the stretching frequencies of active groups in the ir spectra of the complex. The appearance of new bands at 3400 and 1600 cm^{-1} indicate the antisymmetric and symmetric OH stretching and H—OH bending[19], respectively due to coordinated water molecules. A sharp band at 1575 cm^{-1} corresponds to $O-\overset{|}{C}=O$ stretching of the involved acid and clearly indicates the chelation through its COOH group. The coordination of the ligands to the metal ions through N and O is further supported by the appearance of bands at 485 (M—N)[20] and 435 and 360 cm^{-1} (M—O)[20]. Further, the presence of strong bands in the region 1170-1120 cm^{-1} probably indicate the presence of coordinated oxine[21] in the complexes.

Biological studies : Observations on the biocidal activity of the substances are reported in Table 2.

The observation of Table 2 reveals that the complexes have been found to be more active as compared to the free metal and ligands involved. The increased activity of the complex is probably due to their combined activity effect of both the ligands in the metal chelate, due to their more liposoluble nature on being coordinated with the metal ion forming a stable metal chelate or due to a comparatively faster diffusion of the metal complex as a whole through the cells of the fungi which is in accordance with our earlier observations[12,13,22].

Acknowledgement

Authors are grateful to Prof. J. P. Tandon of Rajasthan University, Jaipur and to Dr. S. M. L. Gupta, Head of Chemistry Department, Agra College, Agra for providing facilities.

References

1. J. ELENA and D. GRIGORE, *Ann. Univ. Bucuresti. Chim.*, 1969, **18**, 43.
2. R. C. SHARMA and J. P. TANDON, *Z. Naturforsch.*, 1972, **27**, 308.
3. R. C. SHARMA and J. P. TANDON, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1973, **21**, 757.
4. R. C. SHARMA and J. P. TANDON, *Zh. Chem.*, 1975, **106**, 849.
5. R. C. SHARMA and J. P. TANDON, *Indian J. Chem.*, 1973, **11**, 374.
6. N. S. POLUEKTOVE and R. S. LAUR, *Zh. Neorg. Khim.*, 1970, **15**, 988.
7. H. GERSHON, R. PARMEGIANI and W. J. NICKERSON, *Appl. Microbiol.*, 1962, **10**, 556.
8. H. GERSHON and R. PARMEGIANI, *Appl. Microbiol.*, 1963, **11**, 62.
9. A. ALBERT, S. D. RUBBO, R. J. GOLDACRE and B. G. BALFOUR, *Brit. J. Exptl. Pathol.*, 1947, **28**, 69.
10. J. R. J. SORENSON, *J. Med. Chem.*, 1976, **19**, 135.
11. S. B. PANDHYE and C. R. JOSHI, *J. Inorg. Nucl. Chem.*, 1977, **29**, 1289.
12. R. C. SHARMA, S. P. TRIPATHI, S. KHANNA and R. S. SHARMA, *Curr. Sci.*, 1981, **50**, 748.
13. R. C. SHARMA and S. P. TRIPATHI, *Chem. Era*, in the press.
14. S. P. TRIPATHI, G. K. CHATURVEDI and R. C. SHARMA, *Zh. Chem.*, 1978, **109**, 283.
15. S. P. TRIPATHI, R. C. SHARMA and G. K. CHATURVEDI, *Z. Anorg. Allg. Chem.*, 1980, **462**, 226.
16. N. K. DAVIDNENKO, *Russ. J. Inorg. Chem.*, (*Engl. Transl.*), 1962, **7**, 1412.
17. K. L. MALYAROV and F. P. SUDAKOV, *Russ. J. Inorg. Chem.*, (*Engl. Transl.*), 1961, **6**, 800.
18. G. H. CAREY and A. E. MARTELL, *J. Am. Chem. Soc.*, 1967, **89**, 2859.
19. K. NAKAMOTO, "Infrared Spectra of Inorganic Coordination Compounds", John Wiley, New York, 1970, p. 166.
20. W. SIMON and T. CLERE, "Strukturaufklarung Organischer Verbindungen Mit Spektroskopiechen Methoden", Akademische Verlagsgesellschaft, Frankurt-Am-Main, 1967.
21. R. C. CHARLES, H. FREISER, R. FRIEDEL, L. E. HILLARD and W. D. JOHNSTON, *Spectrochim. Acta*, 1967, **8**, 1.
22. R. C. SHARMA, S. P. TRIPATHI and R. S. SHARMA, *Curr. Sci.*, 1983, **52**, 410.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 850-855

A Study on Solid State Thermal Decomposition Characteristics of Some Metallo-Organic Compounds. Part-II. Thermal Dehydration and Decomposition Characteristics of Some Hydrated Metal Malonates

S. GHOSH*, S. K. RAY**, P. K. RAY and T. K. BANERJEE

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta-700 032

Manuscript received 2 June 1982, revised 4 April 1984, accepted 20 September 1984

Solid state dehydration of the hydrated, Ca, Mn, Co, Ni, Cu and Zn salts of malonic acid and subsequent decarboxylation of the anhydrous salts have been studied by simultaneous DTA TG and DTG techniques. The thermal stability order of the hydrates has been found to be Ni(mal).$2.5H_2O$ > Co(mal).$2H_2O$ > Mn(mal).$2H_2O$ > Zn(mal).$2H_2O$ > Ca(mal).$2H_2O$ > Cu(mal).$2H_2O$. But in the decarboxylation process the trend observed is Ca(mal) > Ni(mal) > Co(mal) > Mn(mal) > Zn(mal) > Cu(mal). Thermal parameters like activation energy, enthalpy change and order of reaction for each process have been computed by standard methods.

Experimental

MALONIC acid used was of L.R. grade and the acid was recrystallised several times from water. The calcium salt was prepared by reacting slight excess of G.R., E. Merck calcium carbonate with the acid in hot aqueous solution, filtration and subsequent crystallisation. The other compounds of malonic acid (those of Co^{II}, Ni^{II} and Cu^{II}) were prepared in a similar manner. The compounds of malonic acid with Mn^{II} and Zn^{II} were prepared by reacting the respective metal carbonates with malonic acid in hot aqueous solution keeping malonic acid in slight excess whereby metal malonates were precipitated. These were filtered, washed with cold water, recrystallised from hot water and finally dried over fused $CaCl_2$.

Simultaneous DTA, TG and DTG determination of the salts were carried out by the procedure described elsewhere[1]. TG curves were utilised for calculating the activation energies of the processes involved, whereas, DTA curves were used to evaluate the enthalpy change accompanying the reactions The initiation, peak and completion temperatures for the dehydration and the decarboxylation processes were noted from the corresponding DTG curves. The hydrated calcium and other metal salts (those of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) as well as their dehydrated varieties were characterised by recording their ir spectra (nujol) on a Beckman IR 20A spectrophotometer by the presence and absence of the ν_{O-H} band in the 3000-3400 cm^{-1} region. All the hydrated and the anhydrous compounds were analysed for their metal contents. For calcium compounds, the calcium content was determined by titration with a standard EDTA solution and for the determination of other metals (Mn, Co, Ni, Cu and Zn), standard methods were used. Carbon and hydrogen were determined by microanalytical techniques. The analytical results are given in Table 1.

TABLE 1—ANALYTICAL DATA OF THE COMPOUNDS

Compound	Analysis % : Found/(Calcd.) M	C	H
$Ca(C_3H_2O_4).2H_2O$	22.38 (22.50)	20.18 (20.21)	3.32 (3.37)
$Mn(C_3H_2O_4).2H_2O$	28.35 (28.47)	18.61 (18.65)	3.05 (3.11)
$Co(C_3H_2O_4).2H_2O$	29.86 (29.92)	18.25 (18.28)	2.98 (3.05)
$Zn(C_3H_2O_4).2H_2O$	32.04 (32.14)	17.68 (17.70)	2.91 (2.95)
$Cu(C_3H_2O_4).2H_2O$	31.50 (31.53)	17.82 (17.86)	2.93 (2.98)
$Ni(C_3H_2O_4).2.5H_2O$	28.49 (28.54)	17.47 (17.50)	3.37 (3.40)

Results and Discussion

On gradual heating from room temperature the hydrated salts were completely dehydrated within the temperature range 112-298°. From the TG, DTG and DTA traces of the dehydration stage it was found that all the metal malonates lost their respective water molecules in a single step excepting those of calcium and copper salts which lost their water molecules in two steps. All these dehydration reactions are presented in Table 2.

**Department of Chemistry, Ramsaday College, Amta, Howrah.

TABLE 2—DEHYDRATION STAGE

Sl. no.	Reaction	Initiation temp. °C	Peak temp. °C	Completion temp. °C	Weight loss % Found/(Calcd.)	E_{act} kcal mol^{-1}	ΔH kcal mol^{-1}	Order of reaction
1.	$Ca(mal).2H_2O \rightarrow Ca(mal).H_2O + H_2O$	118	169	178	10.32 (10.11)	30.28	5.45	1
	$Ca(mal).H_2O \rightarrow Ca(mal) + H_2O$	178	201	236	11.19 (11.25)	39.97	6.68	1
2.	$Mn(mal).2H_2O \rightarrow Mn(mal) + 2H_2O$	150	212	250	18.47 (18.66)	34.48	35.41	1
3.	$Co(mal).2H_2O \rightarrow Co(mal) + 2H_2O$	160	220	250	18.26 (18.28)	37.78	27.1	1
4.	$Ni(mal).2.5H_2O \rightarrow Ni(mal) + 2.5H_2O$	219	271	298	22.08 (21.87)	53.21	31.01	1
5.	$Cu(mal).2H_2O \rightarrow Cu(mal).H_2O + H_2O$	112	122	137	8.88 (8.93)	59.41	8.66	1
	$Cu(mal).H_2O \rightarrow Cu(mal) + H_2O$	137	158	188	10.16 (9.80)		10.07	1
6.	$Zn(mal).2H_2O \rightarrow Zn(mal) + 2H_2O$	138	161	200	17.60 (17.70)	55.30	19.82	1

Initiation, peak and completion temperatures of the dehydration processes, as obtained from the relevant DTG curves, along with the corresponding weight loss are given in Table 2. Enthalpy changes accompanying each dehydration process were determined by standard methods[8] and the activation energies for each dehydration process were computed from an analysis of the corresponding TG curves using the method of Horowitz and Metzger[9]. The $\ln\ln (w_0 - w_f)/(w - w_f)$ *vs* θ plots for the dehydration processes are presented in Fig. 3, while the corresponding plot for decarboxylation reactions are presented in Fig. 4. The orders of both dehydration and decarboxylation reactions were determined by standard methods[3,4] and were found to be unity in all the cases. The results obtained are presented in Table 2 (dehydration) and Table 3 (decarboxylation) and the corresponding curves in Figs. 1 and 2 (dehydration), and Fig. 3. (decarboxylation). Ir spectra of the hydrated and anhydrous varieties were recorded and compared to ascertain the completion of the dehydration process.

Decarboxylation process: All the anhydrous salts exhibit considerable thermal stability and undergo decarboxylation within the temperature range 212°-452°. Initiation, peak and completion

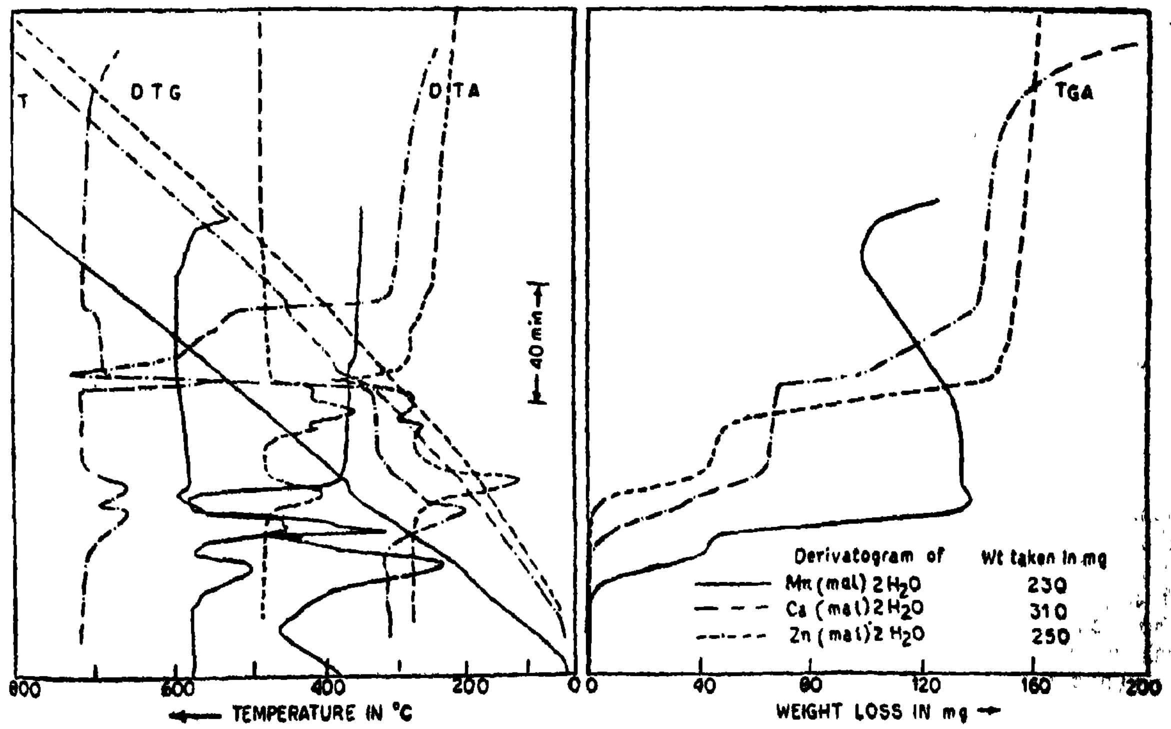


Fig. 1

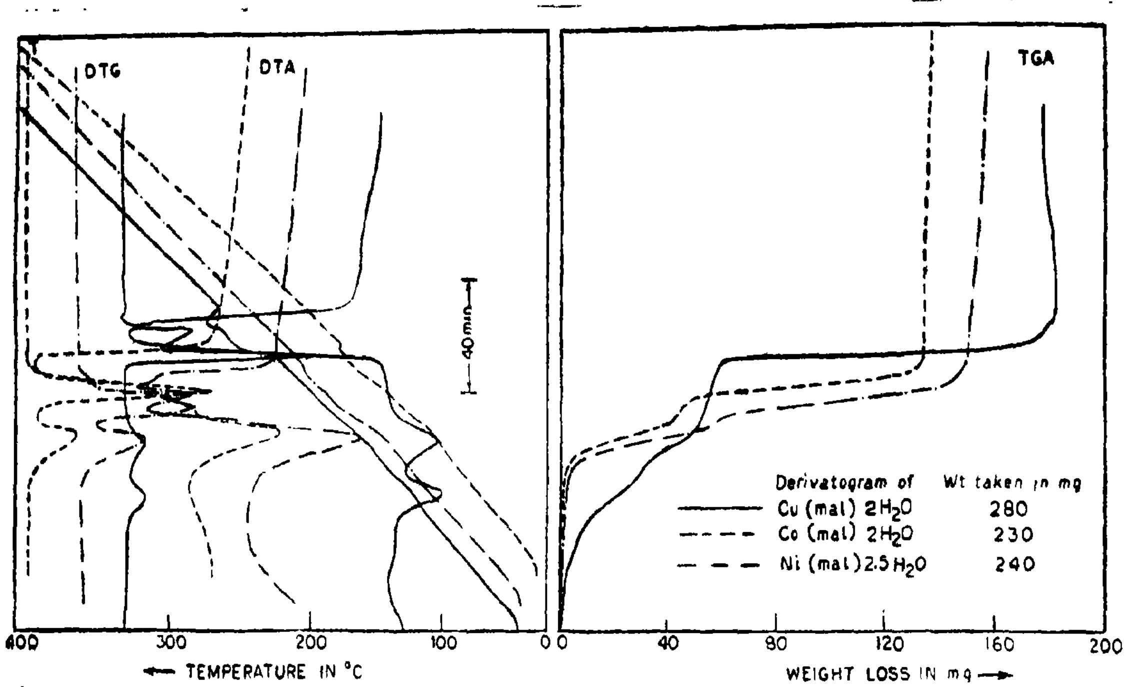


Fig. 2

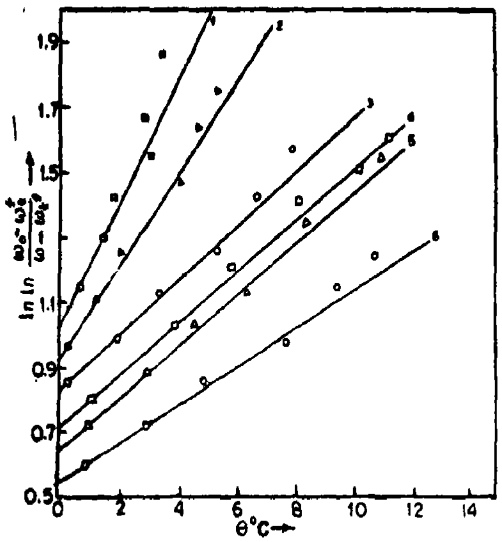


Fig. 3. Plot of lnln $(w_0 - w_f)/(w - w_f)$ *vs* θ for dehydration of metal malonates: (1) Cu(mal).$2H_2O$, (2) Zn(mal).$2H_2O$, (3) Ni(mal).$2.5H_2O$, (4) Co(mal).$2H_2O$, (5) Ca(mal).$2H_2O$ (first stage), and (6) Mn(mal).$2H_2O$.

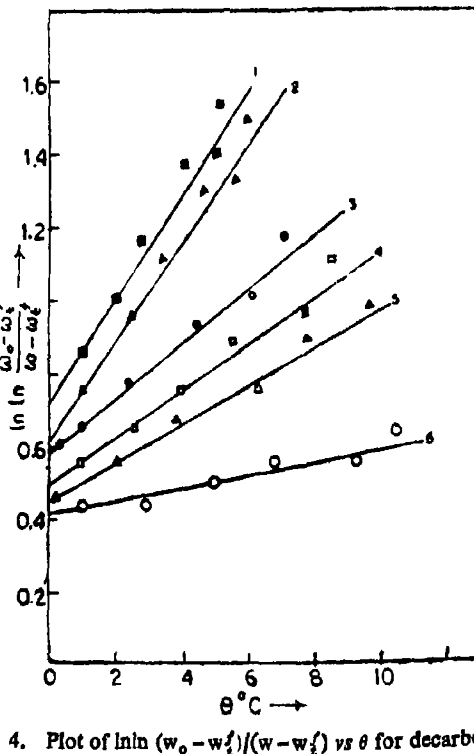


Fig. 4. Plot of lnln $(w_0 - w_f)/(w - w_f)$ *vs* θ for decarboxylation of metal malonates: (1) Cu(mal), (2) Co(ma)l, (3) Zn(mal), (4) Ni(mal), (5) Mn(mal), and (6) Ca(mal).

temperatures for the decarboxylation processes of the anhydrous compounds along with the corresponding weight losses are given in Table 3. The final product left in the crucible was found to be the metallic oxide in all the cases, excepting for calcium malonate where the final product left was calcium carbonate.

The metal oxides being the stable end-products in all the cases, the negative heat of formation of the metal oxides (which varies in the order : MnO> ZnO>NiO>CoO>CuO) may be related to the strength of the M–O bond in the different metal malonates. Hence, the plots of the initiation, peak

TABLE 3—DECARBOXYLATION STAGE

Sl. No	Reaction	Initiation temp. °C	Peak temp. °C	Completion temp. °C	Weight loss % Found/(Calcd.)	E_{act} kcal mol^{-1}	ΔH kcal mol^{-1}	Order of reaction
1.	Ca(mal) → $CaCO_3$ + products	331	358	452	29.75 (29.57)	15.75	106.29	1
2.	Mn(mal) → Mn_3O_4 + products	250	293	370	50.53 (50.35)	34.67	63.43	1
3.	Co(mal) → Co_3O_4 + products	258	294	360	47.25 (47.04)	86.34	75.28	1
4.	Ni(mal) → NiO + products	298	338	390	54.59 (53.51)	49.28	71.89	1
5.	Cu(mal) → CuO + products	212	226	273	53.18 (51.96)	69.44	82.57	1
6.	Zn(mal) → ZnO + products	220	265	314	50.48 (51.38)	43.68	17.40	1

and completion temperatures of thermal decarboxylation of anhydrous metal malonates against the negative heat of formation[8] of the respective metal oxides (Fig. 5) exhibit interesting trends along with the rise of the values of $-\Delta H_f^\circ$. Such variation as reflected in Fig. 5 is close to the behaviour expected from the thermal stability order observed in this study. Only manganese and zinc malonates exhibit departures from this general trend.

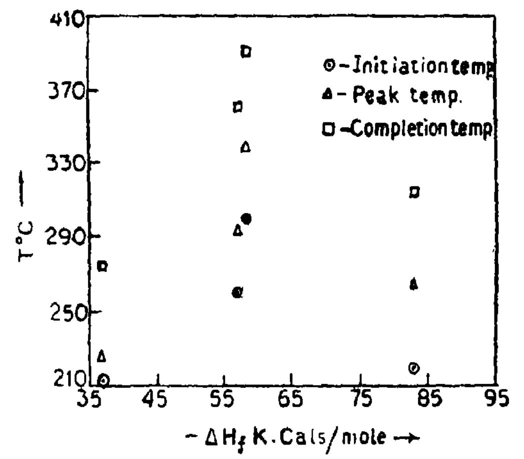


Fig. 5

TABLE 4

Compounds	Initiation temp. °C	Peak temp. °C	Completion temp. °C	ΔH_f° of oxides* kcal mol^{-1}
Mn(mal)	250	293	370	−92.00
Co(mal)	258	294	360	−57.20
Ni(mal)	298	338	390	−58.40
Cu(mal)	212	226	273	−37.10
Zn(mal)	220	265	314	−83.17

* Ref. 13.

The plots of initiation temperature of thermal decarboxylation of the metal malonates against the corresponding reciprocal ionic radii[9] (Fig. 6) exhibit some definite trends. This behaviour is close to the general behaviour of gradual decrease of the stability of metal salts with the decrease in the ionic radii, cobalt and nickel malonates exhibiting departure from this general trend.

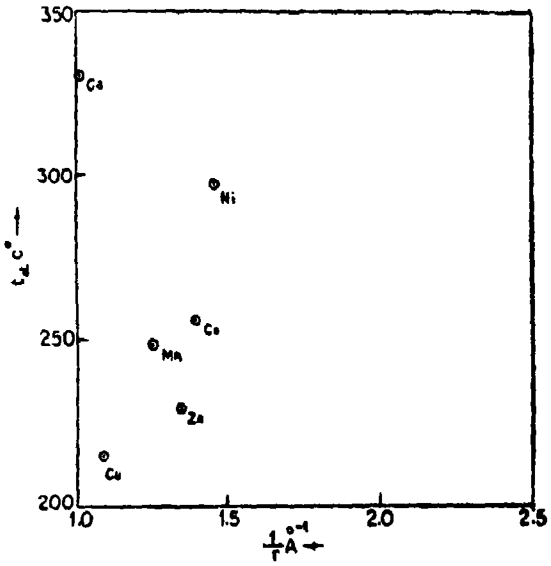


Fig. 6

TABLE 5

Compound	Initial weight loss temp. °C	$\frac{1}{r}$* Å^{-1}
Ca(mal)	331	1.000
Mn(mal)	250	1.219
Co(mal)	258	1.351
Ni(mal)	298	1.428
Cu(mal)	212	1.369
Zn(mal)	220	1.333

*Ref. 14.

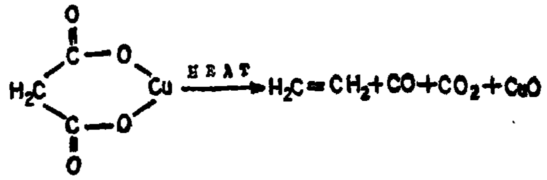
In the single-step dehydration as well as in the first-stage of the two-step dehydration processes, represented by the equations in Table 2, the activation energies are in the order, Cu > Zn > Ni > Co > Mn > Ca, while the overall enthalpy changes for dehydration processes are found to follow the order, Mn > Ni > Co > Zn > Cu >

Ca. The thermal stability of the metal malonate hydrates obtained from the DTG initiation and peak temperatures follow the order, Ni > Co > Mn > Ca > Zn > Cu.

In the decarboxylation of the anhydrous metal malonates represented by equations given in Table 3, the activation energies follow the order, Co > Cu > Ni > Zn > Mn > Ca, while the enthalpy changes for the same process are found to follow the order, Ca > Cu > Co > Ni > Mn > Zn. The thermal stability of the anhydrous metal malonates obtained from the DTG initiation and peak temperatures follow the order, Ca > Ni > Co > Mn > Zn > Cu.

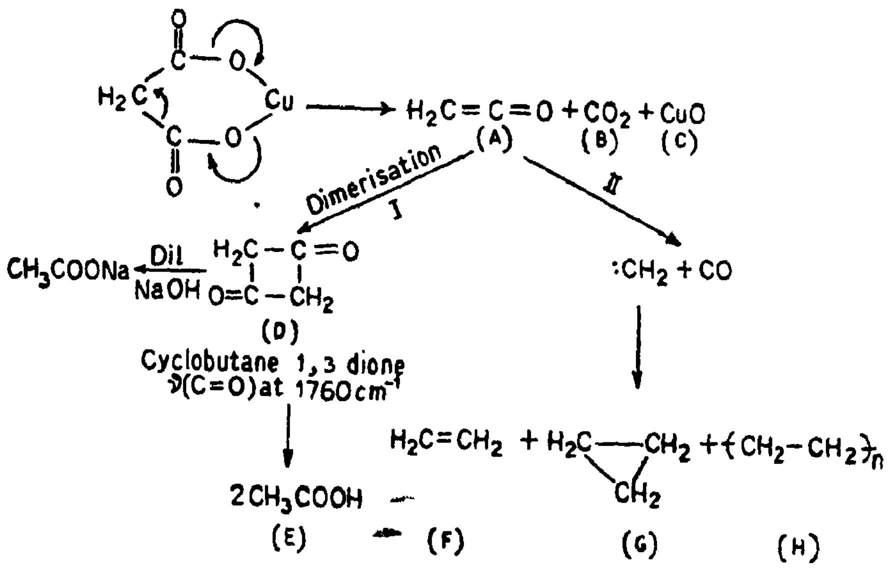
The general series found by Irving and Williams[7] for the stability of complexes in solution is almost the reverse of the above series for the thermal stability in the solid state. The same sequence, as suggested by us, was reported for the thermal stability of other compounds of the same metal ions by earlier workers[8-18]. This behaviour may be accounted for by assuming that the strength of intermolecular bonds play a significant role in determining the thermal stability of compounds in solid state.

In an attempt to study the mode of decomposition of the transition metal malonates, to detect and characterise the decomposition products and to suggest a probable mechanism, copper malonate dihydrate was taken as representative example. This was heated under gradually increasing temperature. At the initiation temperature (212°) for the decarboxylation stage it started decomposing. The process continued for a definite temperature range of 212-273° and became complete at 273° which is exactly its completion temperature. The decomposition process leading to the generation of the heterogeneous products obtained thereof may be represented as



The solid decomposition product was analysed for its copper content and characterised by *X*-ray powder pattern and was found to be cupric oxide. Carbon dioxide was detected by precipitation as calcium carbonate from a solution of calcium hydroxide while carbon monoxide was detected by reduction of iodine pentoxide into iodine, and ethylene was detected by passing the gaseous decomposition products through bromine water and studying the uv spectra of the dibromoethylene produced.

Probable mechanism: On the basis of the different products detected and characterised, it is suggested that the initial decomposition of copper malonate produced CuO, CO_2 and a ketene which is then further decomposed to other products probably through the following Route.



ROUTE-I

ROUTE-II

Route-I: (i) The decomposition products were passed into a trap containing carbon tetrachloride cooled in ice whereby the ketene produced immediately dimerised to produce (D) which was detected by recording its ir spectrum which exhibited the strong carbonyl band in the region 1760-1780 cm^{-1} corresponding to the $\nu_{C=O}$ of the cyclobutane-1,3-dione.

(ii) In another experiment the above CCl_4 solution was shaken with water containing a little NaOH in which the diketone was hydrolysed and formed CH_3COONa. This was evaporated to dryness and

the presence of the $-COO^-$ band was established by ir spectrum.

Route-II : The decomposition products were passed into a ice-cooled trap containing Br_2 in CCl_4 when its yellow colour discharged completely. The CCl_4 solution in the trap was subjected to vapour phase chromatography and the peaks were noted, and compared with an authentic sample of $CH_2Br.CH_2Br$ under similar condition. The presence of $CH_2=CH_2$ was confirmed. Carbon monoxide was detected by the I_2O_5-method and cyclopropane characterised by ir and nmr spectra.

Acknowledgement

The authors are grateful to Dr. N. Ray Chaudhuri and Mr. Sasanka Mukherjee of our department for recording TG, DTA and DTG curves.

References

1. S. Ghosh, S. K. Ray, P. K. Ray and T. K. Banerjee, *J. Indian Chem. Soc.*, 1982, **59**, 1034.
2. K. Sano, *Sci. Rep. Tohuku Univ., Ser. 1*, 1936, **24**, 719.
3. H. H. Horowitz and G. M. Metzger, *Anal. Chem.*, 1963, **35**, 1464.
4. A. W. Coates and J. P. Redfern, *Nature (London)*, 1964, **201**, 68.
5. H. Yokobayashi, K. Nagase and K. Muraishi, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2789.
6. K. Nagase, K. Sato and N. Tanaka, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 439.
7. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.
8. E. Cardarelli, G. D'Ascenzo, A. D. Magri and A. Pupella, *Thermochim. Acta*, 1979, **33**, 267.
9. W. W. Wendlandt and G. R. Horton, *Anal. Chem.*, 1962, **34**, 1098.
10. W. W. Wendlandt, J. H. Van Tossel and G. R. Horton, *Anal. Chim. Acta*, 1960, **23**, 332.
11. G. D'Ascenzo and W. W. Wendlandt, *Anal. Chim. Acta*, 1970, **50**, 79.
12. G. D'Ascenzo, U. Baider Ceipidor and G. De Angelis, *Anal. Chim. Acta*, 1972, **58**, 175.
13. N. A. Hange, "Handbook of Chemistry", 9th ed., Handbook Publishers, Sandusky, 1956, pp. 1590-1605.
14. A. F. Wells, "Structural Inorganic Chemistry", 4th ed., Clarendon Press, Oxford, 1975, p. 259.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 856-858

Stability Constants and Thermodynamic Parameters of Iron(II) Chelates with 2-(Phenylhydrazino)propionic Acid and Their Substituted Derivatives in Aqueous-Ethanol Medium

R. N. KASI VISHWANATHAM and M. G. RAM REDDY*

Department of Chemistry, Osmania University, Hyderabad-500 007

Manuscript received 24 April 1983, revised 5 March 1984, accepted 20 September 1984

The stability constants of Fe^{II} complexes with 2-(Xphenylhydrazino)propionic acids (X = –H, p-CH_3, p-NO_2 and o-CH_3) have been studied with a view to understand the effect of various substitutions present in the ligands. The studies have been carried out potentiometrically in ethanol-water (40%,v/v) medium using Calvin-Bjerrum pH-titration technique as modified by Irving and Rossotti. Thermodynamic parameters have been evaluated and discussed. The effect of dielectric constant on the formation constants has been studied.

THE compounds of substituted phenylhydrazones of pyruvic acid have immense biological and analytical applications[1,2]. Recently, we reported[3] the formation constants of 2-(phenylhydrazino)-propionic acid and its substituted compounds with Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}. The thermodynamic parameters associated with the complexation were evaluated and discussed to explain the nature of bonding. In the present paper results obtained on the proton-ligand and metal-ligand stability constants of 2-(phenylhydrazino)propionic acid, 2-(p-tolylhydrazino)propionic acid, 2-(p-nitrophenylhydrazino)propionic acid and 2-(o-tolylhydrazino)propionic acid with Fe^{II} in various ionic strengths, temperatures and in different ethanol-water mixtures (v/v) employing Calvin-Bjerrum[4,5] pH-titration technique as modified by Irving and Rossotti[6]. In the presence of Fe^{II}, the stability constants were found to be higher than those of the other transition metal ions studied earlier under similar conditions except Cu^{II}. From the formation constants obtained at various temperatures the thermodynamic parameters such as ΔH^{+}, ΔG^{+} and ΔS^{+} have been evaluated and separated into their corresponding electrostatic ($\Delta G_e^{\ddagger}$ and $\Delta H_e^{\ddagger}$) and non-electrostatic or cratic ($\Delta G_c^{\ddagger}$ and $\Delta H_c^{\ddagger}$) components with a view to understand the extent of ionic and covalent nature of the complexes. An attempt has been made to investigate the effect of variation in dielectric constant on the stabilities of complexes in various ethanol-water mixtures.

Experimental

All the chemicals used were either B.D.H. (A.R.) or Merck (G.R.) reagents. The ligands employed were synthesised in our laboratory by known methods[7-10]. As the solubility of the ligands is low in water, the solutions were prepared in 40% (v/v) ethanol-water media. The methods employed to determine the formation constants and the preparation of ferrous nitrate solution in the present work were described in an earlier paper[11]. Since the titrations were carried out in ethanol-water media appropriate pH corrections were applied to the experimentally observed values[12].

Results and Discussion

The proton dissociation constant of the ligands (pKa) and stepwise stability constants log K_1 and log K_2 were calculated using the half-integral method. The stability constants were also evaluated by pointwise and least-square methods and they agree within error limits to that of half-integral method and have been presented in Table 1. Fe^{II} chelates of the ligands showed high stabilities indicating the derivation from the natural order. Similar observations were reported by several workers[13-15] in their study on a number of ligands like 4-hydroxyptoridine, folic acid, riboflavin, pyridine-2-aldoxime, o-phenanthroline, bipyridyl, terpyridyl, *etc*. A unique feature in all these compounds is that they contain one, two or three tertiary nitrogens. The unusual high stability of Fe^{II} chelates were also noted by Irving and Williams[16] and they attributed to the resonance orbital stabilization energy of Fe^{II} complexes upon coordination with a ligand having an aromatic ring system. In the present investigation the ligands possess an aromatic ring system and a tertiary nitrogen which might be responsible for the observed high stabilities.

Effect of ionic strength: To investigate the nature of interactions between the metal ion and ligands the metal-ligand stability constant values were determined at 0.01, 0.05 and 0.1 M ionic strengths at 30°. A study of the dependence of stability constants on ionic strengths showed that

TABLE 1—STEPWISE STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS FOR THE FORMATION OF 1 : 1 AND 1 : 2 Fe^{II} CHELATES AT 30° AND 0.1 *M* IONIC STRENGTH

Ligand	*p*Ka	Stability constant	$-\Delta G^{*}$ kJ mol^{-1}	$-\Delta H^{*}$ kJ mol^{-1}	ΔS J mol^{-1}
2-(Phenylhydrazino)propionic acid	5.15	4.49	26.02	22.38	12.00
		(3.53)	(20.45)	(18.24)	(7.28)
2-(*p*-Tolylhydrazino)propionic acid	5.42	4.56	26.44	22.50	12.97
		(3.94)	(22.84)	(20.33)	(8.28)
2-(*p*-Nitrophenylhydrazino)propionic acid	4.53	3.42	19.83	17.44	7.86
		(2.95)	(17.11)	(15.39)	(5.65)
2-(*o*-Tolylhydrazino)propionic acid	4.85	3.62	21.00	17.65	11.04
		(3.20)	(18.53)	(16.52)	(6.61)

The figures in the parentheses indicate the stability constant and thermodynamic parameters for 1 : 2 complexes. The standard deviation of stability constants is ±0.05. The limit of error for log K values is ±0.05.

there is a regular and slow decrease in the values of stability constants with the increase in ionic strength, which is in agreement with the trend in the variation of *p*Ka values of above ligands. It is seen from Table 1 that the overall stability constants of Fe^{II} chelates follow the order :

2-(*p*-nitrophenylhydrazino)propionic acid < 2-(*o*-tolylhydrazino)propionic acid < 2-(phenylhydrazino)propionic acid < 2-(*p*-tolylhydrazino)propionic acid.

The observed order is in accordance with the electron withdrawing property of nitro group and electron releasing effect of methyl group. The low stability constants observed in the case of 2-(*o*-tolylhydrazino)propionic acid with transition metal ions may be ascribed to steric factors.

Effect of temperature : The values of ΔH^{*}, ΔG^{*} and ΔS^{*} have been calculated from the stability constants obtained at various temperatures at constant ionic strength (0.1 *M*) using Gibbs-Helmholtz equation and are given in Table 1. The ΔH^{*} values were evaluated from the plots of log K *vs* 1/T. The positive slopes indicate that the reactions are exothermic. The ΔG^{*} values are negative for all the chelates showing that these reactions are spontaneous. The exothermic nature of reactions is supported by the negative values of ΔH^{*}. The ΔS^{*} values are positive for all the chelates showing that entropy is favourable for complex formation. The ΔG^{*} and ΔH^{*} were separated into their electrostatic ($\Delta G^{\ddagger}_{e}$ and $\Delta H^{\ddagger}_{e}$) and cratic ($\Delta G^{\ddagger}_{c}$ and $\Delta H^{\ddagger}_{c}$) components in order to know the extent of ionic and covalent nature of bonding in these complexes as suggested by Digischer and Nancollas[14]. Comparison of the electrostatic and cratic components of the thermodynamic parameters from Table 2 for the equilibrium (1)

$$M^{2+}\,(aquo) + L^{-} \rightleftharpoons ML^{+} \quad (1)$$

indicates that $\Delta G^{\ddagger}_{c}$ values are significantly more negative than $\Delta G^{\ddagger}_{e}$ values. This trend suggests that non-electrostatic forces are stronger than the electrostatic forces in 1 : 1 chelates. The data for the equilibrium (2)

$$ML^{+} + L^{-} \rightleftharpoons ML_{2} \quad (2)$$

shows that the 1 : 1 complexes are more favourable than 1 : 2 complexes. Comparison of the difference in the electrostatic and cratic components of Fe^{II} chelates with that of the other transition metal ion complexes reported earlier[8], observes the following order

$$Cu^{II} > Fe^{II} > Ni^{II} > Co^{II} > Mn^{II},$$

which may be due to the anomalous behaviour of stabilities of Fe^{II} complexes.

TABLE 2—ELECTROSTATIC AND CRATIC COMPONENTS OF THERMODYNAMIC PARAMETERS FOR THE FORMATION OF 1 : 1 AND 1 : 2 METAL CHELATES AT 0.1 *M* IONIC STRENGTH

Metal ion : Fe^{II}		Values in kJ mol^{-1}	
Electrostatic components		Cratic components	
$-\Delta G^{\ddagger}_{e}$	$\Delta H^{\ddagger}_{e}$	$-\Delta G^{\ddagger}_{c}$	$-\Delta H^{\ddagger}_{c}$
2-(Phenylhydrazino)propionic acid			
9.87	3.81	26.27	26.15
(8.87)	(3.43)	(21.71)	(21.63)
2-(*p*-Tolylhydrazino)propionic acid			
10.08	3.93	26.53	26.35
(9.08)	(3.56)	(23.89)	(23.76)
2-(*p*-Nitrophenylhydrazino)propionic acid			
9.04	3.47	21.00	20.83
(8.53)	(3.26)	(18.79)	(18.62)
2-(*o*-Tolylhydrazino)propionic acid			
9.71	3.72	21.46	21.29
(8.74)	(3.39)	(19.99)	(19.83)

The figures in the parentheses indicate the values of electrostatic and cratic components for 1 : 2 complexes.

Effect of dielectric constants on stabilities : Another important factor influencing the stability constants of metal chelates are the dielectric constant of the medium and solvating property of the solvent. An attempt has been made to investigate the effect of variation in dielectric constant on the stabilities of complexes of transition metal ions with above ligands in various ethanol-water mixtures (40, 50, 60 and 70%, v/v). The stability constants of the Fe^{II} chelates in different percentages of ethanol-water mixtures are recorded in

TABLE 3—STABILITY CONSTANTS OF Fe^{II} CHELATES IN VARIOUS PERCENTAGES OF ETHANOL-WATER MIXTURES

Ligands	40%	50%	60%	70%
2-(Phenylhydrazino) propionic acid	4.49 (3.53)	4.70 (3.68)	4.92 (3.83)	5.13 (3.96)
2-(p-Tolylhydrazino propionic acid	4.56 (3.94)	4.85 (4.09)	5.07 (4.26)	5.34 (4.39)
2-(p-Nitrophenylhydrazino) propionic acid	3.42 (2.95)	3.58 (3.07)	3.76 (3.20)	3.91 (3.31)
2-(o-Tolylhydrazino) propionic acid	3.62 (3.20)	3.80 (3.34)	3.99 (3.47)	4.17 (3.60)

The figures in the parentheses indicate the values of log K_2.

Table 3. The plots of log K_1 *vs* 1/D are non-linear while the plots of log K_1 and log K_2 *vs* mole fraction showed a good linear relationship. It is seen that with increase in the organic content of the solvent the stability constants increase. This is similar[15] to the ligands containing O-metal links, the stabilities increased by an increase in the organic content of the solvent. However, the reported[16] effect of solvent on complexes containing N-metal links concluded that the organic content of the solvent had little influence on the stabilities of complexes. In the present study of the complexes containing both O-metal and N-metal links the observed increase in the stabilities may be due to the O-metal link which is strongly affected[17].

Acknowledgement

The authors thank Prof. T. Navaneeth Rao, Director, P. G. Courses for helpful discussions, Prof. M. L. N. Reddy, Professor of Chemistry and Prof. C.V. Rathnam, Head, Department of Chemistry of Osmania University for providing facilities. One of the authors (R. N. K.) is thankful to C.S.I.R., New Delhi, for the award of a Senior Research Fellowship.

References

1. S. OBRIV, *Studii. Cercetari. Chim.*, 1957, **5**, 205 (*Chem. Abstr.*, 1968, **52**, 7544).
2. H. PRINGSHEIM and J. LEIBOWITZ, *Berdt. Chem. Caes., Ser. B*, 1923, **56**, 2034.
3. R. N. KASI VISHWANATHAM, K. RAM and M. G. RAM REDDY, *Indian J. Chem., Sect. A*, 1983, **22**, 270.
4. M. CALVIN and K. W. WILSON, *J. Am. Chem. Soc.*, 1945, **67**, 2003.
5. J. BJERRUM, "Metal Amine Formation in Aqueous Solution", P. Haase and Sons, Copenhagen, 1941, p. 298.
6. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
7. A. I. VOGEL, "Practical Organic Chemistry", Longmans, London, 1973, p. 721.
8. W. ROBSON, *J. Biol. Chem.*, 1924, **62**, 504.
9. A. I. VOGEL, "Practical Organic Chemistry", Longmans, London, 1973, pp. 222 and 637.
10. H. MOYER, J. FUGGER and D. LEDNICER, *J. Org. Chem.*, 1956, **21**, 394.
11. V. V. KUMAR, K. RAM, M.G. RAM REDDY, B. SETHURAM and T. N. RAO, *Indian J. Chem., Sect. A*, 1982, **21**, 748.
12. L. G. VAN UITERT and C. G. HAAS, *J. Am. Chem. Soc.*, 1953, **75**, 451.
13. H. IRVING and R. J. P. WILLIAMS, *J. Chem. Soc.*, 1953, 3206.
14. G. DEGISCHER and G. H. NANCOLLAS, *J. Chem. Soc. (A)*, 1970, 1125.
15. L. G. VAN UITERT, W.C. FERNELIUS and B. E. DOUGLAS, *J. Am. Chem. Soc.*, 1953, **75**, 2739.
16. F. BASOLO and R. K. MURMANN, *J. Am. Chem. Soc.*, 1952, **74**, 5243.
17. H. IRVING and H. S. ROSSOTI, *Acta Chem. Scand.*, 1956, **10**, 72.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 859-861

Determination of Relative Stability of Citrato Complexes of Some Metal Ions by Paper Electrophoresis

H. G. MUKHERJEE and SAMIR KANTI DATTA

Department of Pure Chemistry, University College of Science, Calcutta-700 009

Manuscript received 4 October 1983, accepted 20 September 1984

Relative stability of citrato complexes of some transition metal ions, namely Cu^{II}, Co^{II}, Ni^{II} and Zn^{II} have been done by paper electrophoresis using buffer solutions of citric acid and trisodium citrate as carrier electrolyte. Relative stabilities were determined by varying concentration or *p*H of the carrier electrolyte, keeping the ionic strength of the carrier electrolyte constant. From the migration data formation of anionic complexes of probable formula $(MCit)^{2-}$ and $(MCit)^{-}$, where M = Cu^{II}, Co^{II}, Ni^{II} and Zn^{II} and Cit = $C_6H_4O_7/C_6H_5O_7$, were suggested. The order of relative stability of the anionic complexes was found to be $Cu^{II} > Co^{II} > Ni^{II} > Zn^{II}$ which supports the Irving and Williams order of stability of metal complexes with oxygen chelates.

STUDIES on relative stabilities of various metal complexes with tartaric acid, citric acid, tungstic acid by paper electrophoresis have been done by a few workers[1-3]. Recently Mukherjee *et al.*[4] studied relative stability of formato complexes of Fe^{III}, Cu^{II}, Co^{II}, Ni^{II} by paper electrophoresis. This work prompted us to study the relative stability of citrato complexes of Cu^{II}, Co^{II}, Ni^{II} and Zn^{II} by paper electrophoresis.

Experimental

Migrants : 2% solution of $Cu(NO_3)_2.3H_2O$, $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $ZnSO_4.7H_2O$ were used as migrants.

Electrolytes : Stock solutions of trisodium citrate (0.1 *M*), citric acid (0.1 *M*) and sodium nitrate (2 *M*) were prepared as carrier electrolytes and were mixed in different proportions as shown in Tables 1-3. Sodium nitrate was used to maintain the desired ionic strength.

Procedure : Wieland and Fischer[5] type horizontal electrophoretic apparatus was used. Whatman No. 1 (1 cm × 34 cm) paper strips were taken. One drop of each of 2% solution of Cu^{II}, Co^{II}, Ni^{II} and Zn^{II} were electrophorized separately, using different carrier electrolytes mentioned as in Tables 1-3, under the potential difference of 220 V for 1 h. The electrophoretic movements are recorded in Tables 1-3. *p*H of the carrier electrolytes was measured in a Systronics 335 digital *p*H meter using glass electrode. Ionic strength of the carrier electrolytes was kept at 0.5.

Results and Discussion

It appears from Table 1 that Cu^{II} and Co^{II} migrate towards the anode when the concentration of sodium citrate is 0.01 *M* to 0.002 *M*, *p*H of the carrier electrolyte is 7.45-7.20, and at constant ionic strength (0.5). Zn^{II} migrates towards the anode only at high concentration (0.01-0.004 *M*) of sodium citrate when *p*H of the carrier electrolyte is 7.45 to 7.28 and ionic strength is constant. Ni^{II} migrates towards the anode, when the concentration of sodium ctirate is 0 01-0.003 *M*, *p*H of the carrier electrolyte is 7.45-7.22, and ionic strength remaining constant. But when the concentration of sodium citrate falls below 0.004 *M*, Zn^{II} migrates towards the cathode as Zn^{II}-citrate, when it falls below 0.003 *M*, Ni^{II} migrates as Ni^{II}-citrate towards the cathode, and below 0.002 *M* Co^{II} migrates towards the cathode as Co^{II}-citrate. But when the concentration of sodium citrate lies between 0.01 to 0.001 *M*, Cu^{II} migrates towards the anode.

So, by paper electrophoretic study formation of anionic complexes can be predicted. From the resulting data, formation of anionic complexes of Cu^{II}, Co^{II}, Ni^{II} and Zn^{II} of probable formula $(CuCit)^{2-}$, $(CoCit)^{2-}$, $(NiCit)^{2-}$ and $(ZnCit)^{2-}$, where Cit = $C_6H_4O_7$, can be established. Bobtelsky *et al.*[6-7] as well as Dey *et al.*[8] separately suggested the above anionic citrato complexes of Cu^{II}, Co^{II}, Ni^{II} and Zn^{II} at *p*H 6 to 8, which corroborates our study. The data in the Table 1 show that anionic Cu^{II}-citrato complex is more stable than Co^{II}, Ni^{II} and Zn^{II}-citrato complexes and the order of relative stability of the anionic citrato complexes is $Cu^{II} > Co^{II} > Ni^{II} > Zn^{II}$.

Table 2 shows that Cu^{II} behaves as an anionic complex throughout the concentration range (0.025-0 002 *M*) of sodium citrate, when *p*H (4 08) and ionic strength (0.5) of the carrier electrolyte are kept constant. Between the concentration of sodium citrate 0.025 to 0.005 *M*, Co^{II} forms anionic complex, *p*H and ionic strength of carrier electrolyte are

TABLE 1

Sl. no.	Carrier electrolyte	Distance migrated in cm (+, anionic movement ; –, cationic movement)			
		Cu^{II}	Co^{II}	Ni^{II}	Zn^{II}
1.	10 ml 0.1 *M* Na_3-citrate+22 ml 2 *M* $NaNO_3$+68 ml water 0.01 *M* (7.45)*	+3 to +3.7	+2.7 to +3.1	+2.4 to +3.0	+1.0 to +2.1
2.	5 ml 0.1 *M* Na_3-citrate+23.5 ml 2 *M* $NaNO_3$+71.5 ml water 0.005 *M* (7.32)*	+2.7 to +3.2	+2.0 to +2.6	+1.8 to +2.8	+0.7 to +1.8
3.	4 ml 0.1 *M* Na_3-citrate+23.8 ml 2 *M* $NaNO_3$+72.2 ml water 0.004 *M* (7.28)*	+2.5 to +3.1	+1.7 to +2.0	+1.5 to +2.6	+0.4 to +1.7
4.	3 ml 0.1 *M* Na_3-citrate+24.1 ml 2 *M* $NaNO_3$+72.9 ml water 0.003 *M* (7.22)*	+2.1 to +2.8	+1.4 to +1.8	+0.8 to +1.9	–0.3 to –1.7
5.	2 ml 0.1 *M* Na_3-citrate+24.4 ml 2 *M* $NaNO_3$+73.6 ml water 0.002 *M* (7.20)*	+2 to +2.5	+0.7 to +1.1	+0.3 to –2.1	Cationic
6.	1 ml 0.1 *M* Na_3-citrate+24.7 ml 2 *M* $NaNO_3$+74.3 ml water 0.001 *M* (7.08)*	+1 to +2	Cationic	Cationic	Cationic

* Na_3-citrate solution : Concentration (*p*H).
*p*H (7.08–7.45), ionic strength (0.5) constant, Na_3-citrate variable.

TABLE 2

Sl. no.	Carrier electrolyte	Distance migrated in cm (+, anionic movement ; –, cationic movement)			
		Cu^{II}	Co^{II}	Ni^{II}	Zn^{II}
1.	25 ml 0.1 *M* Na_3-citrate+25 ml 0.1 *M* citric acid +20 ml 2 *M* $NaNO_3$+30 ml water (0 025 *M*)*	+3 to +3.1	+2.7 to +3.6	+2.4 to +3.1	+1.8 to +2.8
2.	10 ml 0.1 *M* Na_3-citrate+10 ml 0.1 *M* citric acid +23 ml 2 *M* $NaNO_3$+57 ml water (0.01 *M*)*	+2.7 to +3.8	+2.4 to +3.1	+2 to +2.8	+0.8 to +1.7
3.	5 ml 0.1 *M* Na_3-citrate+5 ml 0.1 *M* citric acid +24 ml 2 *M* $NaNO_3$+66 ml water (0.005 *M*)*	+2.1 to +3.5	+2.0 to +2.8	–1.2 to –2.3	–1 to –2.4
4.	4 ml 0.1 *M* Na_3-citrate+4 ml 0.1 *M* citric acid +24.2 ml 2 *M* $NaNO_3$+67.8 ml water (0 004 *M*)*	+1.9 to +2.9	Cationic	Cationic	Cationic
5.	2 ml 0.1 *M* Na_3-citrate+2 ml 0.1 *M* citric acid +24.6 ml 2 *M* $NaNO_3$, +71.4 ml water (0.002 *M*)*	+1.3 to +2.2	Cationic	Cationic	Cationic

* Concentration of Na_3-citrate in solution.
*p*H (4.08) constant, ionic strength (0.5) constant, citrate variable.

TABLE 3

Sl. no.	Carrier electrolyte	Distance migrated in cm (+, anionic movement ; –, cationic movement)			
		Cu^{II}	Co^{I}	Ni^{II}	Zn^{II}
1.	10 ml 0.05 *M* Na_3-citrate+2 ml 0.05 *M* citric acid +23.55 ml 2 *M* $NaNO_3$, +64.45 ml water (*p*H=5.31)	+1.8 to +2.7	+1.6 to +2.4	+1.4 to +2.1	+1.3 to +2.1
2.	10 ml 0.05 *M* Na_3-citrate+4 ml 0.05 *M* citric acid +23.59 ml 2*M* $NaNO_3$+62.41 ml water (*p*H=5.09)	+1.7 to +2.9	+1.3 to +2.4	+0 8 to +2.0	+0.5 to +2.0
3.	10 ml 0.05 *M* Na_3-citrate+6 ml 0.05 *M* citric acid +23.65 ml 2 *M* $NaNO_3$+60.35 ml water (*p*H=4.83)	+1.5 to +2.6	+0.7 to +1.4	+0.5 to +1.5	+0.2 to +1
4.	10 ml 0.05 *M* Na_3-citrate+8 ml 0.05 *M* citric acid +23.7 ml 2 *M* $NaNO_3$+58.3 ml water (*p*H=4.57)	+1.2 to +2.5	+0.3 to +1.3	Cationic	Cationic
5.	10 ml 0.05 *M* Na_3-citrate+9 ml 0.05 *M* citric acid +23.72 ml 2 *M* $NaNO_3$+57.28 ml water (*p*H=4.33)	+1.2 to +2.5	Cationic	Cationic	Cationic
6.	10 ml 0.05 *M* Na_3-citrate+10 ml 0.05 *M* citric acid +48 ml 2 *M* $NaNO_3$+32 ml water (*p*H=4.08)	+1 to +2.6	Cationic	Cationic	Cationic

Citrate concentration (0.005 *M*) constant. Ionic strength (0.5) constant, *p*H variable.

kept constant. Between the concentration of sodium citrate 0.025 to 0.01 *M*, both Ni^{II} and Zn^{II} form anionic complex, *p*H and ionic strength of the carrier electrolyte remaining the same. From the electrophoretic data, formation of anionic complexes of Cu^{II}, Co^{II}, Ni^{II} and Zn^{II} of probable formula $(CuCit)^-$, $(CoCit)^-$, $Ni(Cit)^-$, $Zn(Cit)^-$, where Cit=$C_6H_5O_7$, as suggested by Bobtelsky *et al.*[6-7] can be predicted. Hence, from the resulting data (Table 2), it can be concluded that the order of relative stability of anionic citrato complexes is $Cu^{II} > Co^{II} > Ni^{II} \approx Zn^{II}$.

Table 3 indicates that Cu^{II} forms anionic complex with the carrier electrolyte throughout the experiment (*p*H 4.08 to 5.31), when ionic strength of carrier electrolyte (0.5) and concentration of sodium citrate (0.005 *M*) are kept constant. Between *p*H 4.57-5.31, Co^{II} forms anionic complex, ionic strength of carrier electrolyte and concentration of

sodium citrate are kept constant. Between pH 4.83 to 5.31, both Ni^{II} and Zn^{II} form anionic complexes, ionic strength of carrier electrolyte and concentration of sodium citrate are kept constant. Here also the anionic complex as $(CuCit)^-$, $(CoCit)^-$, $(NiCit)^-$, $Zn(Cit)^-$ as suggested by Bobtelsky[6,7] can be predicted. So from the resulting data (Table 3) the order of relative stability of the anionic complexes is $Cu^{II} > Co^{II} > Ni^{II} \approx Zn^{II}$.

From the three sets of experimental data it can be concluded that the order of relative stability of the anionic citrato complexes is $Cu^{II} > Co^{II} > Ni^{II} > Zn^{II}$, thereby corroborating to some extent the Irving and William[9] series of stability of metal complexes with oxygen chelates.

Acknowledgement

Authors are thankful to Dr. G. N. Mukherjee, Lecturer, Department of Chemistry, University College of Science for his valuable suggestion during the course of the work.

References

1. B. Hurnik, Theory Struct. Complex Compounds, Papers Symp., Wroclaw, Poland, 1962, p. 693 (Pub. 1964).
2. R. Ripon and Gh. Marcu, *Studii Cercetari Chim.*, 1959, **10**, 201.
3. D. S. Gaibakyan, Z. Z. Termendzhyam and V. M. Tarayan, *Arm. Khim. Zh.*, 1970, **23**, 128.
4. H. G. Mukherjee and A. Devi, *J. Indian Chem. Soc.*, 1982, **59**, 908.
5. T. Wieland and E. Fischer, *Naturwissenschaften*, 1948, 35, 29.
6. M. Bobtelsky and C. Heitner, *Bull. Soc. Chim. Fr.*, 1951, 494.
7. M. Bobtelsky and A. E. Simchen, *Bull. Soc. Chim. Fr.*, 1950, 870.
8. A. K. Dey and S. D. Biswas, *J. Indian Chem. Soc.*, 1965, **42**, 763.
9. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 862-864

Stability Constants of Mercury(II), Copper(II), Lead(II) and Uranium(II)dioxide Complexes with Pyruvate

MAHMOUD GHANDOUR*

Chemistry Department, Faculty of Science (Assiut), Assiut University, Egypt

and

HESHAM MANSOUR and MAHMOUD KHODARY

Chemistry Department, Faculty of Science, (Qena), Assiut University, Egypt

Manuscript received 16 April 1984, accepted 15 August 1984

Potentiometric titration technique is applied to study the complexes of Cu^{II}, Hg^{II}, Pb^{II} and $U^{II}O_2$ with pyruvate at different ionic strengths and temperatures. 1 : 1 metal to ligand complexes are formed with the bivalent copper, mercury and lead ions whereas uranyl ion forms 1 : 1 and 1 : 2 metal to ligand complexes. The thermodynamic functions, $\Delta G°$, $\Delta H°$ and $\Delta S°$ are determined.

THE metal complexes with pyruvate (2-oxopropanoate) are important because of the essential biological role of pyruvic acid. Reports concerning the stiochiometry of the bivalent metal pyruvate complexes are diverse. Complexes of the type ML^+ (L=pyruvate) have been reported with bivalent Cu[1], Mn[2], Pb[3], Ca, Fe and Cd[4]. On the other hand, complexes of the type ML^+ and ML_2 are detected with Cu[5], Ni and Zn[2,6], Pb[7] and UO_2^{2+}[8] ions. It is of interest to investigate the complexes of bivalent Cu, Pb, Hg and UO_2 ions with pyruvate in order to throw more light on the stoichiometry of the complexes and to determine the stability constants and thermodynamic functions.

Experimental

Calvin-Bjerrum's technique as adapted by Irving and Rossotti[9] was used to determine the proton-ligand association constant and formation constants of the pyruvate complexes with Cu^{II}, Hg^{II}, Pb^{II} and $U^{II}O_2$.

*p*H measurements were carried out on Orion Research model 601 digital ionalyzer *p*H meter. Oxygen was removed by bubbling pure nitrogen during titrations. The solutions of $HgCl_2$ (Cambrian), $CuCl_2$ (Prolabo) and $Pb(NO_3)_2$ (B.D.H.) were prepared from the chemically pure grade and titrated complexometrically by EDTA. UO_2Cl_2 (B.D.H.) was prepared and checked as U_3O_8. Solutions of perchloric acid (B.D.H., A.R.) and pyruvic acid (Prolabo) were prepared and standardised alkalimetrically. Sodium perchlorate solution (2 *M*) was used to adjust the ionic strength.

Potentiometric titrations of pyruvic acid (0.03 *M*) in presence of the metal salt solution, the ratio of acid to metal being 6 : 1, were carried out at 25° and at different ionic strengths, *viz.* 0.03-0.11 *M*, using carbonate-free sodium hydroxide solution (0.55 *M*). The titrations were also performed at temperatures ranging from 30 to 50° (μ=0.1) in order to calculate reaction enthalpy and entropy values.

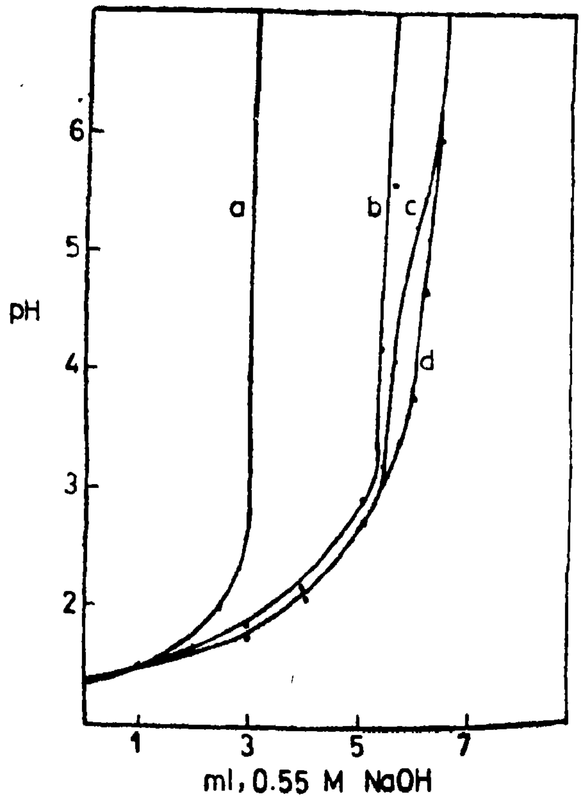


Fig. 1. Titration curves of 50 ml, (a) 0.03 *M* $HClO_4$, (b) a+0.03 *M* pyruvic acid, (c) b+5×10^{-3} *M* Cu^{2+}, (d) b+5×10^{-3} *M* UO_2^{2+} with 0.55 *M* NaOH.

Results and Discussion

The representative curves shown in Fig. 1 indicate that the metal-ligand titration curve is well separated from the ligand titration curve. Thus, replacement of hydrogen ion is due to complexation. It has been noticed that solid phase appeared at pH $\gtrsim$ 5 in the metal-ligand titration curves.

The values of $\bar{n}_A$ (average number of H^+ ions attached per ligand) were plotted against pH. Interpolation at half $\bar{n}_A$ values give the protonation constant of the ligand, log K^H. The log K^H obtained at different ionic strengths at 25° and at different temperatures (μ=0.1) are listed in Tables 1 and 2, respectively.

TABLE 1—FORMATION CONSTANTS (log k) OF PYRUVATE COMPLEXES AT DIFFERENT IONIC STRENGTHS AT 25°

μ M	H^+	Cu^{2+}	Hg^{2+}	Pb^{2+}	UO_2^{2+} K_1	UO_2^{2+} K_2	UO_2^{2+} β
0.0*	2.75	2.14	2.32	2.67	2.39	2.11	4.5
0.03	2.48	1.87	2.10	2.36	2.07	1.86	3.93
0.05	2.38	1.78	1.95	2.16	2.02	1.86	3.88
0.07	2.34	1.70	1.84	2.04	1.93	1.83	3.76
0.09	2.29	1.67	1.69	1.84	1.88	1.80	3.68
0.11	2.20	1.64	1.63	1.72	1.79	1.78	3.57

* Obtained from the linear plots log k *vs* $\sqrt{\mu}$.

TABLE 2—FORMATION CONSTANTS (log k) OF PYRUVATE COMPLEXES AT DIFFERENT TEMP

μ = 0.1 *M* $NaClO_4$

Temp. °C	H^+	Cu^{2+}	Hg^{2+}	Pb^{2+}	UO_2^{2+} K_1	UO_2^{2+} K_2	UO_2^{2+} β_2
30	2.10	1.67	1.69	1.85	1.88	1.81	3.69
35	2.00	1.75	–	–	1.92	1.85	3.77
40	1.95	1.81	1.76	2.07	1.96	1.86	3.82
45	1.85	1.85	–	–	2.05	1.87	3.92
50	1.78	1.89	2.00	2.12	2.11	1.92	4.03

The metal-ligand stability constants were obtained from the curves drawn between $\bar{n}$ (average number of ligands attached per metal ion) and pL (free ligand exponent). The formation of only 1 : 1 complexes of Cu^{II}, Hg^{II} and Pb^{II} were obtained from interpolation at $\bar{n}$=0.5. On the other hand, interpolation at $\bar{n}$=0.5 and 1.5 gave the formation constants of 1 : 1, and 1 : 2 for uranyl pyruvate complexes.

Effect of ionic strength : The stability constants of the metal pyruvate complexes and the protonation constant of pyruvate at different ionic strengths at 25° reveal that log K and log K^H gradually decrease with increasing ionic strength. The thermodynamic stability constants were obtained by extrapolating the linear plots of log K and log K^H *vs* $\sqrt{\mu}$ to zero ionic strength (Table 1). Representative $\bar{n}$ *vs* pL plots are shown in Fig. 2.

Effect of temperature : The log K values, for both pyruvic acid and its metal complexes *vs* 1/T were linear. ΔG^*, ΔH^* and ΔS^* parameters are reported in Table 3. Moreover, the value of the standard free energy was obtained from $\Delta G^\circ = -2.303$ RT log $K^{\mu \to 0}$, where $K^{\mu \to 0}$ is the extrapolated

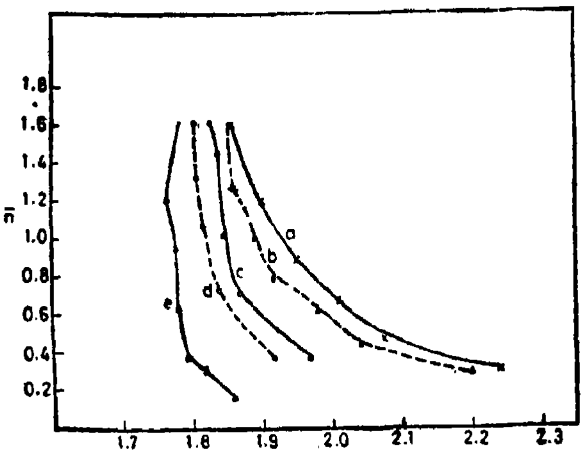


Fig. 2. Formation curves of UO_2-pyruvate complexes at μ (a) 0.03, (b) 0.05, (c) 0.07, (d) 0.09 and (e) 0.11 *M*.

TABLE 3—THERMODYNAMIC PARAMETERS OF PROTONATION AND COMPLEX FORMATION

μ = 0.1 *M*, Temp. 30°

Parameter	H^+	Cu^{2+}	Hg^{2+}	Pb^{2+}	UO_2^{2+}
$-\Delta G^*$ kcal mol^{-1}	2.91	2.32	2.34	2.57	5.11
ΔH^* kcal mol^{-1}	−6.86	4.75	7.63	6.10	7.31
ΔS^* kcal mol^{-1}	−13.04	23.33	32.90	28.61	40.99
$-\Delta G^\circ$ kcal mol^{-1} ($\mu \to 0$)	3.75	2.92	3.75	4.36	6.14

value of the formation constant at zero ionic strength. The order of increase in ΔS^* values is the same as that of formation constants. The formation constants are seen to be larger at 50° than at 30° (Fig. 3). Endothermic heats are not uncommon in reactions where electrostatic interactions predominate[8]. On the other hand, HL formation constant seems to be exothermic.

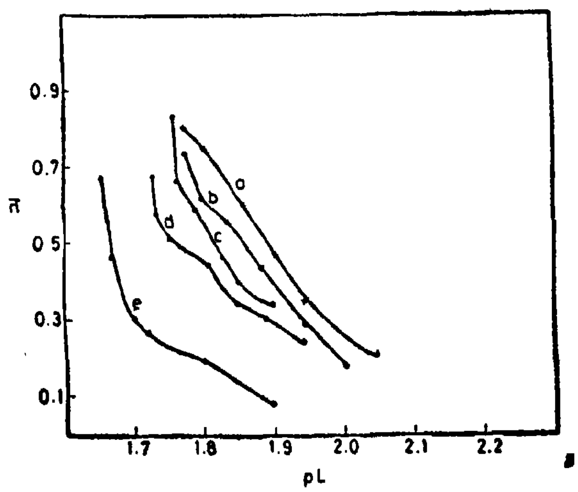


Fig. 3. Formation curves of Cu-pyruvate complex at (a) 50°, (b) 45°, (c) 40°, (d) 35° and (e) 30°.

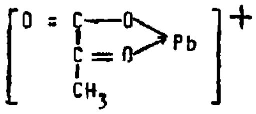
According to the data obtained by Dazzi and Falqui[3], the protonation of the ligand is endothermic and the formation of lead pyruvate complex is exothermic. The only difference in the experimental condition is the use of 1.0 M KNO_3. However, our results are in accordance with those obtained by Leussing and Shultz[2] concerning the effect of temperature on the protonation of pyruvate anion and some metal pyruvate complexes.

Comparing the values of pK_a for pyruvic acid at 25°, reported earlier, *viz.* 2.40 (3 M $NaClO_4$)[4], 2.20 (0.3 M $NaClO_4$)[4], 2.49 ($\mu \rightarrow 0$)[10], 2.35 (0.5 M KCl)[11], 2.39 (0.65 M KCl)[9], 2.10 (M NaCl)[12] and 2.34 (M KNO_3)[3], with those obtained in the present investigation indicates their reliability.

Thus, in water pyruvic acid forms 1 : 1 metal to ligand complexes with Cu^{II}, Hg^{II} and Pb^{II} ions. The results are in accordance with those reported earlier[1,8] for Cu^{II} and Pb^{II} pyruvate complexes. The formation of 1 : 1 and 1 : 2 uranyl pyruvate complexes is confirmed[1,8].

However, the formation of other complexes with 1 : 2 metal to ligand ratios were reported[6,7] for Cu^{II} and Pb^{II}. No datum is available for Hg^{II} pyruvate complexes for comparison. It has been shown that other bivalent metal cations, such as Mn, Ca, Fe and Cd form but weaker 1 : 1 metal pyruvate complexes[9,4].

It was proved[3] by chemical and spectrometrical data that the structure of the PbL^+ complex forms a five-membered ring consisting of carboxylic group, the metal ion and the oxo group, *viz.*



It is assumed that the same structure can be formulated for the other 1 : 1 bivalent metal complexes with pyruvate.

References

1. S. RAMAMOORTHY, A. RAGHAVAN, V. R. VIJAYARAGHAVAN and M. SANTAPPA, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1851.
2. D. L. LEUSSING and D. C. SCHULTZ, *J. Am. Chem. Soc.*, 1964, **86**, 4846.
3. E. DAZZI and M. T. FALQUI, *Gazz. Chim. Ital.*, 1976, **106**, 1095.
4. O. FORSBERG, B. GELLAND, P. ULMGREN and O. WAHLBERG, *Acta Chem. Scand., Ser. A*, 1978, **32**, 345.
5. E. GELLES and R. W. HAY, *J. Chem. Soc.*, 1958, 3673.
6. D. E. TALLMAN and D. L. LEUSSING, *J. Am. Chem. Soc.*, 1969, **91**, 6253.
7. B. LENARCIK and Z. WARNKE, *Rocz. Chem.*, 1969, **43**, 1329.
8. S. RAMAMOORTHY and M. SANTAPPA, *Curr. Sci.*, 1968, **37**, 403.
9. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
10. K. J. PEDERSON, *Acta Chem. Scand.*, 1952, **6**, 243.
11. D. L. LEUSSING and E. M. HANNA, *J. Am. Chem. Soc.*, 1966, **88**, 693.
12. D. E. TALLMAN and D. L. LEUSSING, *J. Am. Chem. Soc.*, 11969, **91**, 6253.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 865-869

Hydration Energies of Gas Phase Polyatomic Ions and Molecules—A CNDO/2 Approach

S. C. RAKSHIT* and BANI MUKHERJEE

Chemistry Department, Burdwan University, Burdwan-713 104

Manuscript received 17 April 1982, revised 23 December 1983, accepted 20 September 1984

The published results of *ab initio* calculations of solvation energies[1] of a number of species lead to certain general trends with the help of which many of the energy components occurring in the Daudel's symbolic expression[2] for hydration energy can be estimated. This feature, coupled with Born's free energy of transfer from vacuum to solvent medium within the frame work of CNDO/2 molecular orbital charge distribution, enables the calculation of hydration energy. Radius adjustment, which is an accessory encumbrance in any electrochemical calculation, is made in a very general manner.

THE problem of solvation and free energy changes on transfer of ions from one dielectric medium to another has been probed theoretically and experimentally[3]. Attempts at formulation of expressions of hydration energies have been made at various levels of sophistication. Previous relations[4-8] have invariably been accompanied, in practice, by assumptions of (i) increased value of the radius on hydration, (ii) discrete or continuum nature of the dielectric environment permitting the use of adjusted dichotomy or nondichotomy of dielectric constant values, and (iii) in many cases, the stereodispositions of the hydration ligands[5,6] and the interatomic distances. More recent formulations, falling within the area of quantum machinical self consistent field theories, involve 'supermolecule' approach[1], local field theories[9], 'solvaton' approach[10] and perturbation effect due to polarisability of the environment[11].

Our approach is an adaptation of Hoijtink *et al.*[12] within the framework of CNDO/2 m.o. theory for calculation of the main contribution towards the hydration energy of gas phase polyatomic ions or molecules. The total hydration energy break-up (Daudel[2]) is given as

$$\varepsilon_s = \varepsilon_{sc} + \varepsilon_{so} + (\varepsilon_{se} + \varepsilon_{sp} + \varepsilon_{sd}) + \varepsilon_{sa} \qquad (1)$$

where ε_{sc} = Cavitation energy during solvation.

ε_{so} = Energy of partial orientation of solvent molecules not in the primary solvation sheath.

ε_{se}, ε_{sp} and ε_{sd} = Electrostatic interaction energies of charging, polarisation of the environment and dispersion energy, respectively.

ε_{sa} = Anisotropic interaction energy in solvation responsible for dipolar binding of solvent molecules at localised points of the solute = primary hydration energy.

The present method consists of the following steps.

1. The CNDO/2 technique[13] is employed to find the resultant net atomic charge distributions in the ions or molecules in the gaseous state with the individual radii values, r_i's and interatomic distances, r_{ij}'s.

2(a). We shall treat water-cluster to consist of tetrahedron of five water molecules as has very often been used in the past. A tetrahedron is first dissociated into five water molecules (energy ε_1 per molecule) and 'n' number out of these five, necessary for primary hydration of each solute (ion or molecule) are evaporated (energy ε_2 per molecule) to create a cavity in the bulk. The remaining (5-n) molecules participate in tetrahedral formation with the rest of the bulk solvent causing an exothermic energy of binding ε_3 per molecule. Thus, $5\varepsilon_1 + n\varepsilon_2 + (5 - n)\varepsilon_3 = \varepsilon_{sc}$ of Daudel expression (equation 1).

(b). The solute molecule (or ion) in the gaseous equilibrium configuration is approached by 'n' number of H_2O molecules to form a hydrated species in gas phase state. The energy involvement will be ε_4 (exothermic) and is identifiable with ε_{sa} of equation 1.

(c). During such exothermic interactions, there will be some polarisation of charges in the gas phase species accompanied by dilations of bonds. The endothermic energy involvement ε_5 per ion may be viewed as the perturbation due to the dipolar field of the H_2O molecules in the primary hydration layer. This perturbational energy ε_5 is not present in equation 1, but is a feature of the 'solvaton' model[10].

(d). The hydrated gas phase species is transferred from vacuum to the bulk solvent to occupy the cavity. The relation $\varepsilon_e = \varepsilon_{se} + \varepsilon_{sp}$, utilises CNDO/2 molecular orbital charges[13] at different

atom centres of the polyatomic ion or molecule together with the adjusted values of atomic radii in hydrated state (equation 3).

(e). If the hydrated species is an ion, there will be further secondary hydration. For each of the 'n' number of proton-donor or -acceptor hydrating molecules in the primary layer, there would exist about the same number of hydrating molecules in the secondary hydration sheath. These additional 'n' molecules are made avialable from rupture of a tetrahedron (endothermic ε_1 per molecule) and involve a low net energy of interaction[1], ε_7 per molecule of water, for its orientation in the secondary layer. Thus, $n(\varepsilon_1+\varepsilon_7)$ equals ε_{s0} of Daudel expression. For neutral molecule there is little possibility[1] of any secondary hydration.

After thus identifying the different energy terms with the various Daudel terms qualitatively, it is now necessary to quantify the terms for final formulation of hydration energy which is

$$N\varepsilon_s = N(\varepsilon_{s0}+\varepsilon_{sa}+\varepsilon_{sO}+\varepsilon_{se}+\varepsilon_{sp})+N\varepsilon_5 = N[5\varepsilon_1 + n\varepsilon_2+(5-n)\varepsilon_3]+Nn\varepsilon_4+Nn(\varepsilon_1+\varepsilon_7)+N\varepsilon_6+N\varepsilon_5 \qquad (2)$$

$$\quad\text{I} \qquad\qquad\qquad \text{II} \qquad\qquad \text{III} \qquad\quad \text{IV} \quad \text{V}$$

where N is the Avogadro number.

Let us now consider the net contribution by the energy terms I, II and III (equation 2) for polyatomic ions and molecules separately. For ions $N\varepsilon_2=-N\varepsilon_3=6.1$ kcal mol^{-1} (both by CNDO/2 and *ab initio* supermolecule approach), $N\varepsilon_1$= enthalpy of vaporisation of water=9.8 kcal mol^{-1}, $N\varepsilon_4=-20$ kcal mol^{-1} (*ab initio* supermolecule approach). $N\varepsilon_7$, secondary hydration energy, can be reasoned out to be around $2\sim3$ kcal mol^{-1}. Thus for mono to pentahydration, the net energy contribution coming from I, II and III (Table 1) is about -3 kcal mol^{-1} which being small, may be neglected.

TABLE 1

Energy in kcal g ion^{-1}

n	I $-N\varepsilon_{s0}$	II $-N\varepsilon_{sa}$	III $-N\varepsilon_{s0}$	I+II+III
5	+79.5	-100.0	+18.0	-2.5
4	+63.6	-80.0	+14.4	-2.0
3	+47.7	-60.0	+10.8	-1.5
2	+31.8	-40.0	+7.2	-1.0
1	+16.2	-20.0	+3.6	-0.5

Therefore, for ions

$$\Delta E_{hydrn} = N\varepsilon_s \approx N\varepsilon_6 + N\varepsilon_5$$
$$= -N\,1/2\,(1-1/D)\sum_{A,B} q_A q_B \Gamma_{AB} + 7.5/Z/ \qquad (2a)$$

where the first term is the Born term equivalent[12] in CNDO/2 theory and the second one the perturbational energy term*, Z being the valence of the ion.

For molecules, an analysis of the energy terms in equation 2 leads to (i) neglect of $N\varepsilon_5$, (ii) neglect of secondary solvation $n(\varepsilon_1+\varepsilon_7)$, (iii) anisotropic interaction energy $N\varepsilon_{sa}=N\varepsilon_4=-8.5$ kcal mol^{-1}. The reason for neglecting the first is that for neutral molecules global charge transfer from the species to the hydration layer is not large rendering a very small effective polarisation due to perturbation (step 2c).

Since the secondary hydration of neutral molecules should be very small, the second factor is neglected. The third factor of anisotropic energy value for neutral molecules varies from -6 to -11 kcal mol^{-1} of the hydrating molecules. It is much smaller than the corresponding ionic term (-20 kcal mol^{-1}) and the average is around -8.5 kcal mol^{-1}. Working within the framework of these assumptions, it is shown (Table 2) that the energy terms I and II of equation 2 (III has been set equal to zero) lead to definite but different endothermic values for uncharged molecules for mono- to pentahydration in the primary layer.

TABLE 2

Energy in kcal mol^{-1}

n	I	II	I+II
5	+79.5	-42.5	+37.0
4	+63.6	-34.0	+29.6
3	+47.7	-25.5	+22.2
2	+31.8	-17.0	+14.8
1	+16.2	-8.5	+7.7

Equation 2a and Table 1 enable us to write for polyatomic ions

$$\Delta E_{hydrn} = -627.1\left[\frac{1}{2}\sum_i \frac{q_i^2}{R_i} + \sum_{i<j}\sum \frac{q_i q_j}{R_{ij}}\right]\left(1-\frac{1}{D}\right) + 7.5/Z/ \text{ kcal mol}^{-1} \qquad (3)$$

where the CNDO/2 molecular orbital atomic charges q_i, q_j's, the effective atomic radii and interatomic distances R_i, R_{ij}'s in the hydrated state are in atomic units, and D=78.5 at 25°.

The relations $R_i=r_i+pr_w$, and $R_{ij}=r_{ij}+qr_w$ are used in equation 3 where r_w is radius of water molecule (a.u.), and p and q are the radius adjustment factors, taken to be 0.5 and 1.0, respectively. A general CNDO/2 criterion for p, q values is set up later. The r_{ij}, R_i and R_{ij} data are internally calculated by the computer with instructions for original geometry and for r_i, r_j, p and q fed into it. Table 3 based on equation 3 comprises data for hydration energies of gas phase polyatomic ions.

We now turn to neutral molecules. Equation 2a and Table 2 permit us to write

$$\Delta E_{hydrn} = N\varepsilon_6 + 7.4n \text{ kcal mol}^{-1} \qquad (4)$$

where 'n' is the number of hydrating molecules (1 to 5) in the primary sheath. If the hydration

* Hydration energies of gas phase monovalent ions is around 70 to 100 kcal g ion^{-1} ; perturbational energy can hardly exceed 5 to 10% of the actual. Hence, the setting of $N\varepsilon_6 = 7.5/Z/$ represents an average value.

TABLE 3

Polyatomic ion	Hydration energy kcal mol^{-1}	
	Calcd. value from Eqn. (3) (1 a.u = 627.1 kcal mol^{-1})	Literature value
Formate	−97.2	–
Fluoroformate	−101.65	–
Chloroformate	−91.06	–
Acetate	−90.56	–
Monofluoroacetate	−88.82	−92.60
Difluoroacetate	−90.95	−86.60[a]
Trifluoroacetate	−95.86	–
Monochloroacetate	−86.1	−88.20[a]
Dichloroacetate	−83.5	−83.10[a]
Propionate	−88.40	–
Ammonium	−81.29	−(72.5±5.5)[b,c]
Nitrate	−78.59	−75.01[b]
Nitrite	−88.5	−96.75[b]
Chlorate	−87.24	−83.14[b]
Sulphate	−254.6	−253.0[b]
Sulphite	−328.1	–
Bisulphide	−84.52	−79.65[b]
Thiocyanate	−76.01	−74.06[b]
Carbonate	−317.1	−313.9[b]
Methoxide	−84.29	–
Ethoxide	−78.34	–
Isopropoxide	−73.93	–
t-Butoxide	−70.49	–

[a]P. Haberfield and A. K. Rakshit, *J. Am. Chem. Soc.*, 1976, 98, 4393.
[b]Ref. 8. [c]Ref. 7.

number 'n' obtained by 'supermolecule approach' for any organic molecule be taken to be the same for other members of the same class (such as open chain carboxylic acids or amides or esters), then ΔE_{hydrn} can be easily evaluated (Table 4) using the Born type expression with CNDO/2 charge distribution.

$$\Delta E_{hydrn} = \left\{-627.1\left[\left(\sum_i \frac{q_i^2}{2r_i} + \sum_{i<j}\sum \frac{q_i q_j}{r_{ij}}\right)\left(1-\frac{1}{D}\right)\right] + 7.4n\right\} \text{ kcal mol}^{-1} \quad (5)$$

In equation 5 one is to use the same r_i and r_{ij} as in the equilibrium configuration and no adjustment in radius value is made since the perturbational energy ($N\epsilon_s$) has already been set equal to zero. A few trials show that the results can also be computed with the help of Born type expression alone where radius adjustments are made, $R_i = r_i + pr_w$, and $R_{ij} = r_{ij} + qr_w$, with p, q values being 1 and 2, respectively.

$$\Delta E_{hydrn} = N\epsilon_s \text{ (adjusted)} = -627.1\left[\left(\sum_i \frac{q_i^2}{(r_i + pr_w)} + \sum_{i<j}\sum \frac{q_i q_j}{r_{ij} + qr_w)}\right)\left(1-\frac{1}{D}\right)\right] \quad (6)$$

TABLE 4

Molecule	$N\epsilon_s$	7.4n	Hydration energy (kcal mol^{-1})		
			Calculated from Eqn. (5)	Calculated from Eqn. (6)	Literature value
Formic acid	−36.3	29.6	−6.7	−12.47	−9.97[a]
Fluoroformic acid	−60.14	37.0	−23.14	−22.08	–
Chloroformic acid	−47.16	29.6	−17.56	−16.54	–
Acetic acid	−42.33	29.6	−12.73	−14.74	−10.20[a]
Monofluoroacetic acid	−49.0	29.6	−19.4	−15.73	−17.04
Difluoroacetic acid	−60.14	37.0*	−23.14	−19.94	−17.89[c]
Trifluoroacetic acid	−76.52	37.0*	−39.52	−26.78	–
Monochloroacetic acid	−48.35	29.6	−18.75	−15.97	−15.16[c]
Dichloroacetic acid	−45.34	29.6	−15.83	−14.75	−16.16[c]
Formamide	−38.50	29.6	−8.9	−13.34	≈ −13.36[a]
Acetamide	−43.14	29.6	−13.54	−14.91	−12.03[a]
Propionamide	−43.46	29.6	−13.86	−15.30	−18.11[a]
Methyl formate	−27.47	22.2**	−5.27	−11.25	−8.16[a]
Ethyl formate	−28.28	22.2**	−6.08	−11.83	−8.33[a]
Methyl acetate	−35.05	22.2**	−12.85	−13.69	≈ −12.02[a]
Methyl alcohol	−13.36	11.1†	−2.26	−4.07	−11.38[a] −10.98[a]
Ethyl alcohol	−13.48	11.1†	−2.38	−4.45	−12.22[a]
Isopropyl alcohol	−14.61	11.1†	−3.5	−4.91	−14.33 (20°)[a,b] −13.33 (B.P.)[a,b]
t-Butyl alcohol	−14.8	11.1†	−3.7	−5.12	−14.43 (25°)[a,b] −12.71 (B.P.)[a,b]

*For fluoroformic, difluoroacetic and trifluoroacetic acid,, n = 5. **For esters, n = 3. †For alcohol set, due to low energy of interaction of one of the two hydrating units, the hydration number 'n' has been set equal to 1.5.

[a]"Handbook of Chemistry and Physics", ed. R. C. Weast, 59th. ed., 2nd Printing, C. R. C. Press, Florida, 1979, C-730, C-722, C-723 ; "International Critical Tables", Vol. 5, McGraw-Hill, New York, 1929, pp. 136 (Table C), 148 (Table 1). [b]J. A. Riddick and E. E. Toops, Jr., "Organic Solvents", Interscience Publishers, New York, 1955. [c]P. Haberfield and A. K. Rakshit, *J. Am. Chem. Soc.*, 1976, 98, 4393.

TABLE 5—CHARGE DISTRIBUTION CRITERION FOR CLASSIFICATION INTO DIFFERENT (p, q) PAIRS

Species Molecule Ion	Amount of (+) ve charge on the central atom ( ) in a.u.	Amount of total (−) ve charge of the atoms on the surface of the sphere in a.u *	Surface density of (−) charge on the surface of the sphere in a.u./sq. Å	$\rho \times 10^2$	p, q values
CO_3^{2-}	0.4032 (C)	2.4032 (O, O, O)	0.1131	28.05	0.5, 1
NCS^-	0.1118 (C)	1.1118 (N, S)	0.0365	32.63	0.5, 1
$HCOO^-(COO^-)$	0.3894 (C)	1.1606 (O, O)	0.0591	15.17	0.5, 1
$FCH_2\overset{*}{C}OO^-(\overset{*}{C}OO^-)$	0.3408 ($\overset{*}{C}$)	1.1150 (O, O)	0.0550	16.13	0.5, 1
$ClCH_2\overset{*}{C}OO^-(\overset{*}{C}OO^-)$	0.3681 ($\overset{*}{C}$)	1.1052 (O, O)	0.0545	14.80	0.5 1
CH_3O^-	0.1594 (C)	1.1594 (O, H, H, H)	0.0464	29.10	0.5, 1
ClO_3^-	0.3893 (Cl)	1.3893 (O, O, O)	0.0448	11.51	0.5, 1**
NO_3^-	0.6361 (N)	1.6361 (O, O, O)	0.0877	13.79	1, 2**
$FCOO^-$	0.5214 (C)	1.1585 (O, O)	0.0590	11.31	0.5, 1**
SO_4^{2-}	1.1223 (S)	3.1223 (O, O, O, O)	0.1200	10.67	1, 2
$\overset{*}{H}COOH$ (−COOH)	0.3721 (C)	0.5487 ($\overset{*}{H}$, O, O)	0.0236	6.34	1, 2
$\overset{*}{C}H_3COOH$ (−COOH)	0.3930 (C)	0.6769 ($\overset{*}{C}$, O, O)	0.0233	5.93	1, 2
$F\overset{*}{C}H_2COOH$ (−COOH)	0.3684 (C)	0.4112 ($\overset{*}{C}$, O, O)	0.0142	3.84	1, 2
$Cl\overset{*}{C}H_2COOH$ (−COOH)	0.4140 (C)	0.5629 ($\overset{*}{C}$, O, O)	0.0194	4.68	1, 2
$\overset{*}{C}H_3\overset{*}{C}H_2OH$	0.1663 (C)	0.3381 ($\overset{*}{C}$, $\overset{*}{H}$, $\overset{*}{H}$, O)	0.0113	6.81	1, 2
$\overset{*}{C}H_3CONH_2$ ($-CONH_2$)	0.3677 (C)	0.6881 ($\overset{*}{C}$, N, O)	0.0243	6.61	1, 2
$\overset{*}{C}H_3COOCH_3$ ($-COOCH_3$)	0.4007 (C)	0.6425 ($\overset{*}{C}$, O, O)	0.0227	5.66	1, 2

Species having (p, q) values (0.5, 1) : *Ions* : formate, fluoroformate, chloroformate, acetate, monofluoroacetate, difluoroacetate, trifluoroacetate, monochloroacetate, dichloroacetate, propionate, methoxide, ethoxide, isopropoxide, t-butoxide, chlorate, thiocyanate, nitrite, sulphite, carbonate, bisulphide.

Species having (p, q) values (1, 2) : *Ions* : nitrate, sulphate ; *Molecules* : acids : formic, fluoroformic, chloroformic, acetic, monofluoroacetic, difluoroacetic, trifluoroacetic, monochloroacetic, dichloroacetic, propionic ; alcohols : methyl, ethyl, isopropyl, t-butyl ; amides : formamide, acetamide, propionamide ; esters : methyl formate, ethyl formate, methyl acetate.

*Ligand atoms in parenthesis. **Buffer zone, trials with (p, q) needed.

The relation 6 removes the necessity of any preknowledge of 'n', the hydration number in the primary layer.

Table 4 speaks for itself. However, the calculated values of hydration energy for the alcohol set seem to be off by about −8.0 to −10.0 kcal/mol^{-1}. But the calculated values refer to monomeric forms of alcohols whereas the literature values, evaluated from the thermodynamic data of the relevant enthalpy terms, are not exclusive of the effect of existence of dimers. Hence, the apparent deviations in case of alcohols, shown in Table 4 are largely illusory.

We would complete our discussion by setting up a charge distribution criterion for assigning (p, q) values in radius adjustment. We have seen that only two pairs of values, (0.5, 1.0) and (1.0, 2.0), can cover a wide selection of ions and molecules. We assume a sphere of effective radius drawn around the central atom of the ion (such as N atom in NO_3^-) and compute the surface density of the charges due to directly linked ligand atoms if these charges were smeared on the spherical surface. For neutral molecule, one is to choose that one as the central atom the neighbourhood of which is likely to be the zone of primary hydration (*e.g.* carbon atom of the carboxylic group of an acid). For any particular species, the ratio ρ, of this surface charge density to the central charge is calculated and few such sample data (recorded as $\rho \times 10^2$) are given in Table 5.

When the ratio $(\rho \times 10^2) > (12.5 \pm 1.5)$, the (p, q) pair are (0.5, 1.0) and where it is less the (p, q) pair are (1.0, 2.0). There are a few species (*e.g.* NO_3^-, fluoroformate *etc.*) for which the values fall in buffer zone (*viz.* 12.5 ± 1.5). Trial calculations made with the one or the other (p, q) pair show one of these two to conform to literature values.

Below Table 5 there appear different species (ions and molecules) which are thus classified under the two (p, q) types. This criterion cuts across the division of species into ions and molecules and accounts for using the same (p, q) values for SO_4^{2-}, NO_3^-, acetic acid and alcohols. This charge criterion, therefore, helps in bringing into order much of the confusion over radius adjustment of ions and molecules in solution.

References

1. A. PULLMAN in "Quantum Theory of Chemical Reactions", eds. R. DAUDEL, A. PULLMAN, L. SALEM and A. VEILLARD, D. Reidel Publishing Co, Boston, 1981.
2. R. DAUDEL in "Quantum Theory of Chemical Reactivity", D. Reidel Publishing Co., Boston, 1973, p. 81.
3. S. C. LAHIRI and S. ADITYA, *J. Indian Chem. Soc.*, 1979, **56**, 1112.
4. T. J. WEBB, *J. Am. Chem. Soc.*, 1929, **48**, 2589.
5. L. I. ANTROPOV, "Theoretical Electrochemistry", Mir Publishers, Moscow, 1972, pp. 80, 82.
6. D. D. ELEY and M. G. EVANS, *Trans. Faraday Soc.*, 1938, 34, 1093.
7. H. F. HALLIWELL and S. C. NYBERG, *Trans. Faraday Soc.*, 1963, 59, 1126.
8. D. W. SMITH, *J. Chem. Educt.*, 1977, **54**, 540.
9. O. TAPIA in "Quantum Theory of Chemical Reactivity", D. Reidel Publishing Co., Boston, 1973, p. 25.
10. G. KLOPMAN, *Chem. Phys. Lett.*, 1967, **1**, 200.
11. R. CONSTANCIEL in "Quantum Theory of Chemical Reactivity", D. Reidel Publishing Co., Boston, 1973, p. 73.
12. G. J. HOIJTINK, E. DE BOER, P. H. VAN DER MEIJ and W. P. WEIJLAND, *Recl. Trav. Chim. Pays-Bas*, 1956, 75, 487.
13. J. A. POPLE, D. P. SANTRY and G. A. SEGAL, *J. Chem. Phys.*, 1965, 43, S136 ; J. A. POPLE and D.L. BEVERIDGE, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 870-871

Studies in Lanthanide Ions Complexes with Some Substituted Sulphonic Acids

A. S. WANKHADE, B. G. KHOBRAGADE and M. L. NARWADE*

Department of Chemistry, Government Vidarbha Mahavidyalaya, Amravati-444 604

Manuscript received 17 September 1983, revised 1 August 1984, accepte September 1984

The interaction of lanthanide ions (Ca^{III}, Ce^{III}, Pr^{III}, Nd , Sm^{III} and Gd^{III}) with some substituted sulphonic acids such as (i) 1,2-dihydroxybenzene-3,5-disulphonic acid (1,2 DHB-3, 5DSA), (ii) 6,7-dihydroxynaphthalene-2-sulphonic acid (6,7-DHN-2SA), (iii) 8-amino-1-naphthol-5,7-disulphonic acid (8A-1N-5,7-DSA), (iv) 8-amino-1-naphthol-3,6-disulphonic acid (8A-1N-3,6-DSA), (v) 8-amino-1-naphthol-3,5-disulphonic acid (8A-1N-3,5-DSA), (vi) 8-amino-1-naphthol-5-sulphonic acid (8A-1N-5SA), (vii) 7-amino-1-naphthol-3-sulphonic acid (7-A-1N-3SA), (viii) 2-aminobenzenesulphonic acid (2A-BSA), and (ix) 2-amino-4-methyl-5-chlorobenzenesulphonic acid (2A-4M-5Cl-BSA) have been investigated at 30° and $\mu = 0.1$ *M* ($NaClO_4$) by Calvin-Bjerrum technique La^{III}, Ce^{III}, Pr^{III} and Gd^{III} form 1 : 1 and 1 : 2 complexes but Nd^{III} and Sm^{III} form only 1 : 1 complex with all the sulphonic acids. The validity of log K = a*p*k + b relation is examined for these complexes.

SHERRY *et al.*[1] have investigated lanthanide complexes with carboxylic acids. Ramamoorthy and Manning[2] studied exhaustively the mixed ligand chelates of meso-di-tartaric acid with divalent and trivalent metals. Recently, Darnall and Birnhaum[3-4] showed that lanthanide ions could substitute for calcium ion and produce an active enzyme system. Considering the biological significance of lanthanide ions, the present work is aimed at investigating the complexing ability of substituted sulphonic acids with lanthanide ions.

Experimental

The purity of the substituted sulphonic acids (Schuchardt, Germany) were checked by their melting points. Lanthanide perchlorates were prepared by the standard procedure. All the solutions were prepared in double-distilled water. The details of the *p*H measurements and other chemicals are given in an earlier paper[5].

Results and Discussion

The dissociation constants of the sulphonic acids and stability constants of the simple complexes were evaluated by the method of Irving and Rossotti[6] (Tables 1-4). It could be seen from Tables 2-4 that La^{III}, Ce^{III}, Pr^{III} and Gd^{III} form 1 : 2 complexes with most of the sulphonic acids while Nd^{III} and Sm^{III} form only 1 : 1 complexes with all ligands (sulphonic acids).

The stability constants for the 1 : 1 complexes for various rare earth ions have been plotted against e^2/r. For the calculation of e^2/r values of crystal radii of rare earth ions have been taken from the literature[7]. The plots of $\log K_1$ *vs* e^2/r show a linearity except in the case of 8A-1N-5, 7-DSA chelates.

Validity of $\log K = apk + b$ *relation*: This relation was tested for lanthanide complexes of sulphonates of 8-amino-1-naphthols. These complexes generally obey the linear relationship. In this particular case pK_2 and not (pK_1 + pK_2) is taken on Y axis. This is because of the fact that the lanthanide complexes of 8A-1N

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS (*p*K) OF SUBSTITUTED SULPHONIC ACIDS

Sl. no.	Ligand	pK_1	pK_2
1.	1,2-DHB-3,5-DSA	7.86±0.04	12.60
2.	6,7-DHN-2SA	8.10±0.03	12.15
3.	8A-1N-5,7-DSA	2.90±0.05	8.60±0.05
4.	8A-1N-3,6-DSA	3.91±0.06	9.37±0.07
5.	8A-1N-3,5-DSA	3.08±0.06	8.64±0.04
6.	8A-1N-5SA	3.15±0.04	9.12±0.05
7.	7A-1N-3SA	3.68±0.06	9.52±0.04
8.	2A-BSA	2.88±0.02	–
9.	2A-4M-5Cl-BSA	2.60±0.01	–

TABLE 2—METAL-LIGAND STABILITY CONSTANTS

Sl. no.	Ligand	La^{III}		Gd^{III}	
		$\log k_1$	$\log k_2$	$\log k_1$	$\log k_2$
1.	1,2-DHB-3,5-DSA	13.21	11.40	13.34	8.90
2.	6,7-DHN-2SA	–	–	10.03	7.23
3.	8A-1N-5,7-DSA	4.42	3.13	4.22	3.00
4.	8A-1N-3,6-DSA	6.19	5.19	5.69	5.29
5.	8A-1N-3,5-DSA	4.70	3.20	8.04	5.61
6.	8A-1N-5SA	5.98	5.74	5.48	4.85
7.	7A-1N-3SA	5.48	3.90	5.88	–
8.	2A-BSA	6.90	5.13	2.00	–
9.	2A-4M-5Cl-BSA	7.80	6.03	7.23	–

TABLE 3—METAL-LIGAND STABILITY CONSTANTS

Sl. no.	Ligand	Pr^{III} log k_1	Pr^{III} log k_2	Ce^{III} log k_1	Ce^{III} log k_2
1.	1,2-DHB-3,5-DSA	5.00	4.15	8.10	4.02
2.	6,7-DHN-2SA	5.12	4.51	5.12	4.01
3.	8A-1N-5,7-DSA	4.60	3.06	4.92	3.62
4.	8A-1N-3,6-DSA	6.29	5.49	–	–
7.	7A-1N-3SA	–	–	9.12	7.10
8.	2A-BSA	1.79	1.07	2.20	1.52

TABLE 4—METAL-LIGAND STABILITY CONSTANTS

Sl. no.	Ligand	Sm^{III} log K_1	Nd^{III} log K_1
1.	1,2-DHB-3,5-DSA	13.44	6.04
2.	6,7-DHN-2SA	10.93	10.43
3.	8A-1N-5,7-DSA	4.02	4.62
4.	8A-1N-3,6-DSA	5.89	5.99
5.	8A-1N 3,5-DSA	4.50	4.80
6.	8A-1N-5SA	6.00	6.11
7	7A-1N-3SA	5.68	5.98
8.	2A-BSA	2.01	2.20
9.	2A-4M-5Cl-BSA	7.30	7.10

sulphonates are generally formed around *p*H 6.0 at which the NH_3^+ group is completely dissociated.

The slope values from the various plots of pK_2 *vs* log K_1 of 1 : 1 complexes are given below.

Metal ion complexes—	La^{III}	Nd^{III}	Sm^{III}	Gd^{III}
Slope values	– 1.66	1.75	1.87	1.68

Jones *et al.*[8] suggested on the basis of purely electrostatic model that the slope will increase with increasing cationic charge and decreasing the distance of separation. In the case of substituted 8A-1N complexes of rare earths, the observed slope values are higher than those for the transition metal complexes. This is expected to give a higher value for the slope. The observed values are, therefore, justifiable in the light of Jones *et al.* suggestion.

Acknowledgement

Authors are grateful to the Principal, Vidarbha Mahavidyalaya, Amravati for providing the facilities.

References

1. A. D. SHERRY, C. YOSHIDA. E. R. BIRNBAUM and D. W. DARNALL, *J. Am. Chem. Soc.*, 1973, **95**, 3011.
2. S. RAMAMOORTHY and P. G. MANNING, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1977, 1988, 1997.
3. D. W. DARNALL and E. R. BIRNBAUM, *J. Biol. Chem.*, 1970, **245**, 6484.
4. D. W. DARNALL and E. R. BIRNBAUM, *Bio-chemistry*, 1973, **12**, 489.
5. M. L NARWADE and D. V. JAHAGIRDAR, *J. Indian Chem. Soc.*, 1974, **51**, 1008.
6. T. T. MOELLER, D. F. MARTIN, L. C. TOMPSON R. FERRUS, G. R. GEISTEL and W. J. RANDALL, *Ch m. Rev.*, 1965, **1**, 65.
7. F. A. COTTON, "Advanced Inorganic Chemistry", Interscience, New York, 1967, p. 1052.
8. J. G. JONES, J. B. POOLE, J. C. TOMKINSON and R. J. P. WILLIAMS, *J. Chem. Soc.*, 1958, 2001.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 872-875

Studies on Polybasic Acid Character of Some Hydrogen Vermiculites and Chlorites

M. ADHIKARI, M. K. MAJUMDAR and A. K. PATI

University College of Agriculture, 35 Ballygunge Circular Road, Calcutta-700 019

Manuscript received 19 July 1983, accepted 20 September 1984

The nature and strength of acidity of colloidal acid clays isolated from some interstratified silicate minerals, vermiculites and chlorites, have been investigated electrometrically. The differences in the polybasic acid character on ageing are also reported. The chemical stability and multiple acid character depend on chemical composition, degree of lattice substitution and net negative charge in unit cell.

EXTENSIVE studies[1-8] have been made on the electrochemical character of colloidal acid clays belonging to layer lattice silicate minerals, kaolinites, illites, montmorillonites *etc.* Such studies are useful for (i) identification of clay minerals in soils, sedimentary rocks, *etc.*, and (ii) control of soil acidity by necessary soil amendments (cf. lime treatment) Previous studies[4,5,7] on acid clays have differentiated between two types of soil acidity, (a) active acidity (lower pK values) due to H_3O^+, $Al(H_2O)_6^{3+}$ and (b) potential or latent acidity (higher pK values) due to monomeric and polymeric hydroxy Al, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_6(OH)_{15}^{3+}$ and some other hydrolysis products of exchangeable Al with divergent pK values. On prolonged storage, acid character profoundly changes and becomes complicated due to the formation of multiple acid species of different acid strength[8]. Although much work has been done on this aspect, more data are desirable, specially, with respect to interstratified minerals, commonly found in soils and sedimentary rocks. With this objective, an investigation was undertaken for vermiculite and chlorite minerals to characterise (i) different types of acidity (*cf.* acid strengths and free energy changes of neutralisation of reacting acid species) in acid clays, (ii) changes in acidity on storage, and to correlate, (iii) acid characters with variations in chemical composition.

Experimental

Materials : The clay samples taken in this study were (i) vermiculites from Bagespura (Karnataka), Malavangatta (Karnataka) and Ranchi (Bihar), and (ii) chlorites from Kulu (Himachal Pradesh) and Nainital (Uttar Pradesh). These samples were collected from regions of different climatic zones as well as different geological setting and rock types of India.

Methods 1 : Clay fractions ($< 2\ \mu$) were isolated from powdered natural samples by the usual process of dispersion and sedimentation[9], and were converted into homoionic H-form by passing through ion-exchange resin (Amberlite IR-120, H-form). The base exchange capacity (B.E.C.) values of these clays were determined by the standard procedures[7]. The structural formulae[1] for the clay minerals in the samples were determined from chemical analyses[10] and are shown in Table 1.

The clay mineral components[11] of these samples were identified by X-ray data as Vermiculite with traces of interstratefied vermiculite illite in Bagespura. Vermiculite with traces of illite vermiculite intergrades in Malavangutta, octahedral mica type biotite in Ranchi, and chloride with traces illite in Kulu.

TABLE 1 – STRUCTURAL FORMULAE OF H-CLAYS

Bagespura H-clay	$[(Si_{5.51}\ Al_{2.26}\ Fe^{3+}_{.23})\ (Fe^{2+}_{.86}\ Fe^{3+}_{1.56}\ Ti_{.24}\ Mg_{3.42})\ (Na^{+.51}_{.08}\ K_{.48})\ O_{20}\ (OH)_4]^{-.72}\ H^{+.72}$
Malavangatta H-clay	$[(Si_{5.78}\ Al_{2.22})\ (Al_{.25}\ Fe^{2+}_{.86}\ Fe^{3+}_{1.67}\ Ti_{.29}\ Mg_{2.80})\ (Na^{+.58}_{.08}\ K_{.48})\ O_{20}\ (OH)_4]^{-.46}\ H^{+.46}$
Ranchi H-clay	$[(Si_{6.67}\ Al_{1.33})\ (Al_{1.27}\ Fe^{2+}_{.84}\ Fe^{3+}_{.61}\ Ti_{.18}\ Mg_{2.81})\ (Na^{+.43}_{.05}\ K_{.87})\ O_{20}\ (OH)_4]^{-.87}\ H^{+.87}$
Nainital H-clay	$[Si_{6.72}\ Al_{1.28})\ (Al_{2.62}\ Fe^{2+}_{1.1}\ Fe^{3+}_{1.47}\ Ti_{.24}\ Mg_{.92})\ (Na^{+.11}_{.07}\ K_{.04})\ O_{20}\ (OH)_{16}]^{-.15}\ H^{+.15}$
Kulu H-clay	$[Si_{7.04}\ Al_{.96})\ (Al_{3.08}\ Fe^{2+}_{1.1}\ Fe^{3+}_{.86}\ Ti_{.95}\ Mg_{4.91})\ (Na^{+.46}_{.30}\ K_{.2})\ O_{20}\ (OH)_{16}]^{-.18}\ H^{+.18}$

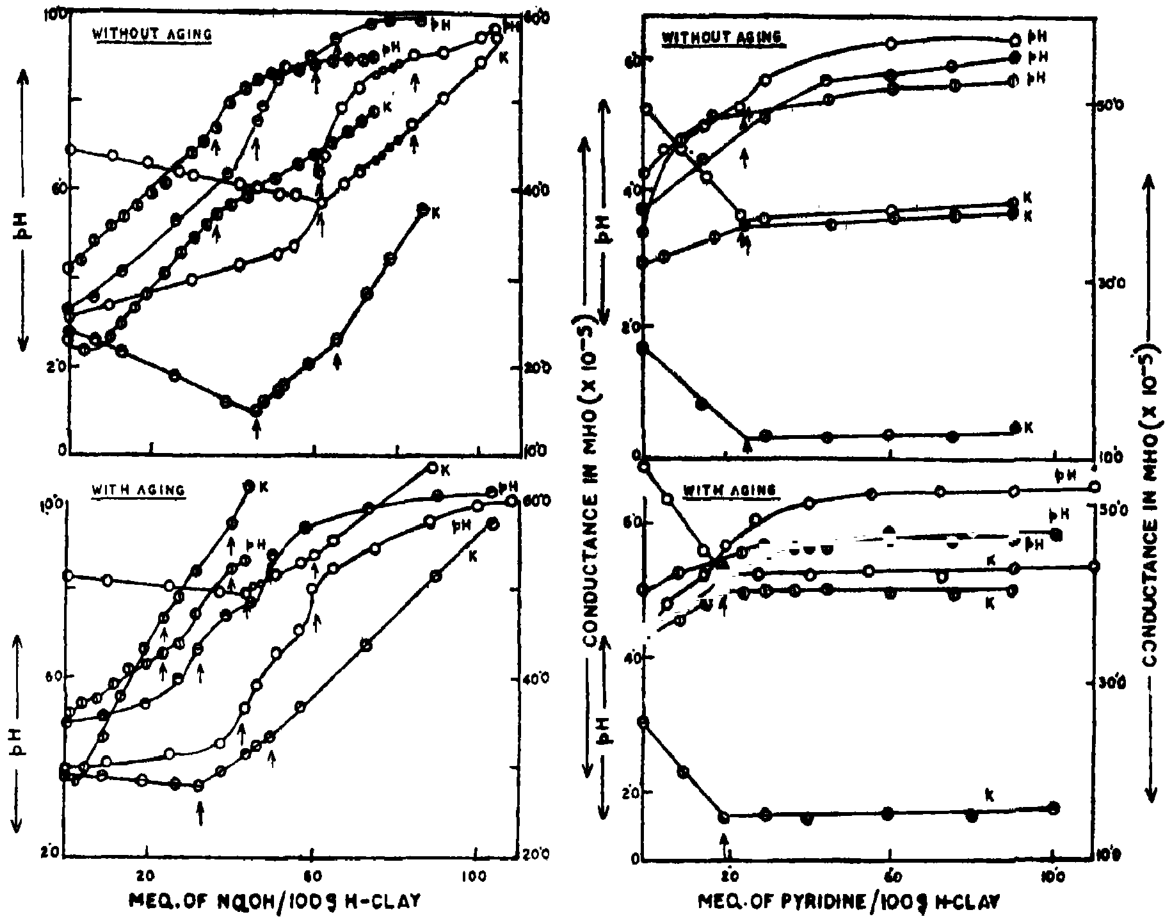


Fig. 1. Alkali and pyridine titration curves of H-clay from Bagespura (O—O), Malavangatta (⊖—⊖), and Ranchi (⊕—⊕) samples.

Method 2 : For alkali titrations, freshly prepared H-clay suspensions were equilibrated in a thermostatic bath at 30 ± 0.5° for 24 h in separate Jena flasks with increasing amount of 0.02 *N* NaOH (total volume 50 ml having 0.6% colloid (clay) content) and the *p*H and conductance values were measured by Elico glass electrode *p*H meter and Systronic conductivity bridge, respectively. For pyridine titration, freshly prepared H-clay suspensions were equilibrated similarly for 24 h with increasing amount of 0.1 *N* pyridine solution. The *p*H and conductance values were measured as before[7,11]. The clay suspensions were allowed to age at room temperature for 75 days. Electrometric titrations of aged clays were performed with both alkali and pyridine. The free energy changes of neutralisation (ΔF_H) of clay acids at 30° were calculated from the equation[7]

$$\Delta F_H = 1395\ (14.14 - pH).$$

The results of various electrometric titrations are shown in Figs. 1 and 2, and Tables 2 and 3.

Results and Discussion

The electrometric titrations of acid clays with strong and weak base are summarised in Tables 2 and 3 and illustrated in Figs. 1 and 2. The salient features of these findings are:

(i) Neutralisations of fresh acid clays (both vermiculites and chlorites) with strong base show two inflexion points in *p*H curves and two breaks in conductance curves, indicating dibasic acid character. The order of acid strength is of the sequence, Bagespura (*p*H 3.1, pK_1 4.0), Malavangatta (*p*H 3.37, pK_1 5.0), Ranchi (*p*H 4.27, pK_1 5.75), Nainital (*p*H 4.37, pK_1 6.15) and Kulu (*p*H 4.8, pK_1 6.55). Lattice substitution of Al for Si in tetrahedral silica sheet is 31.1 (Bagespura), 27 7 (Malavangatta), 16.6 (Ranchi), 16 (Nainital) and 12% (Kulu). Hydrogen clays are unstable and spontaneously change to H-Al system. The quantity of Al release and subsequent conversion to hydroxy-Al species in acid clays varies depending on the mineralogical make up and degree of interstratification (Table 1). First inflexion points (*p*H 6.5-8.65) are mostly due to

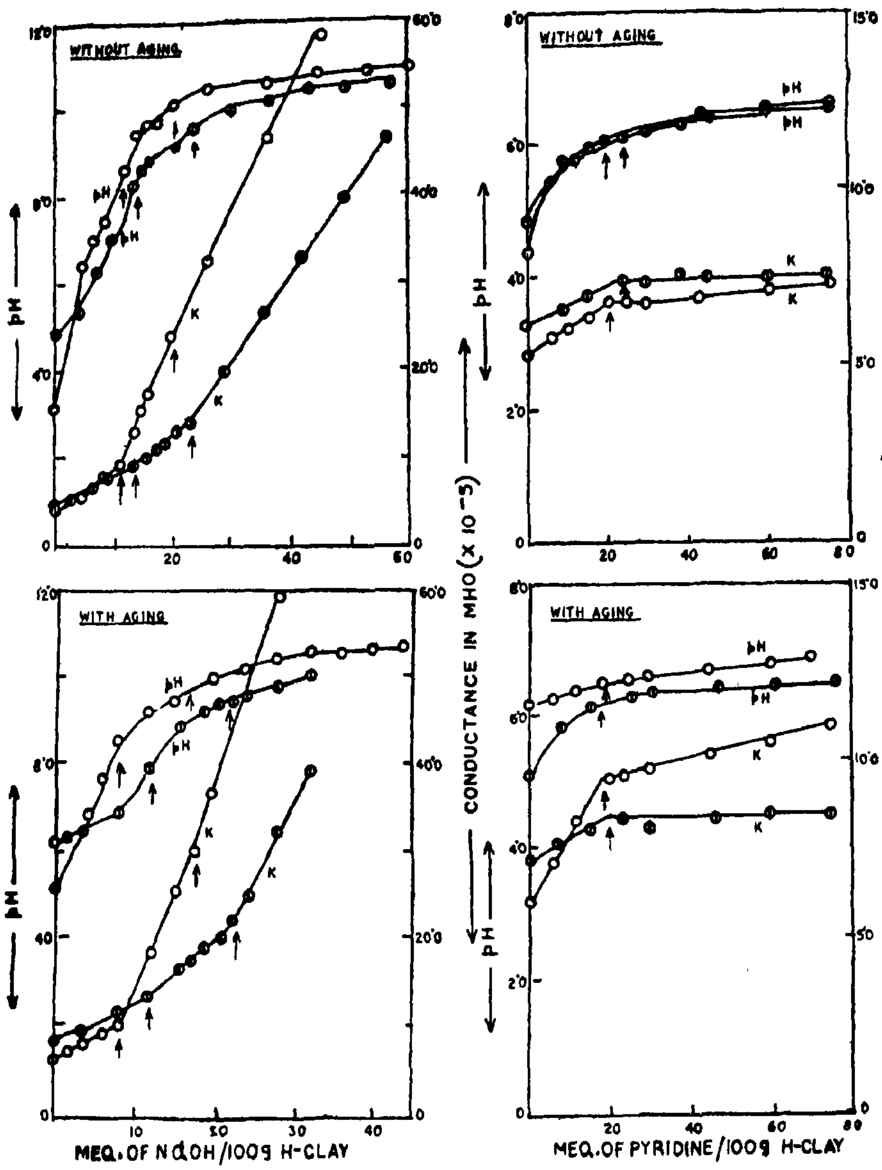


Fig. 2. Alkali and pyridine titration curves of H-clay from Kulu (O—O) and Nainital (◐—◐) samples.

neutralisation of active acid species, H_3O^+, $[Al(H_2O)_6]^{3+}$, and the second inflexion points are observed at higher *p*H value (9.0-11.5) due to neutralisation of latent acid species of different hydroxy-Al. Free energy changes ($\triangle F_H$) with neutralisation of active acid species is more than that of the corresponding neutralisation of potential acid species. On storage of acid clays, active acidity (exchangeable) decreases and potential (non-exchangeable) acidity increases. The *p*H of aged vermiculite clay sols change to 4.05-5.0, and that of aged chlorite clay sols increase to 5.15-6.1. The inflexion points in neutralisation of aged clay sols are observed at lower *p*H values in comparison to fresh clay sols. A composite mixture of hydroxy Al, Fe and Mg cover non-exchangeable sites in planar and broken edge surfaces and the total titrable acidity decreases. Higher pK_a values of acid chlorite sols indicate that the amount of poly-aluminohydronium cations formation is greater in chlorites than in vermiculites.

(ii) Electrometric titrations of acid clays with a weak base, pyridine (Table 3), show only one inflexion in *p*H curve and one break in conductance curve. Pyridine (pK_b=8.8) can neutralise active acidity (H_3O^+) but not the hydroxy Al species, monomeric and polymeric. From the inflexion points in *p*H curves and breaks in conductance curves, net Al release and chemical stability of acid

TABLE 2—ALKALI TITRATION DATA

Clay sample	B. E. C. meg/ 100 mg	Lattice substitution	Initial pH value (0.6% suspension	At first inflexion point and break				At second inflexion point and break			
				pH	Meq. of NaOH/100 g H-clay	pK_1	ΔF_H kcal mol^{-1}	pH	Meq. of NaOH/100 g H-clay	pK_2	ΔF_H kcal mol^{-1}
Bagespura H-clay	78.0	31.1	3.10	6.5	61.0	4.0	10.66	9.0	84.0	4.3	1.17
Bagespura aged clay	–	–	4.05	5.3	43.0	4.25	–	8.0	60.0	4.35	–
Malavangatta H-clay	49.92	27.7	3.37	7.6	46.0	5.0	9.13	9.4	66.0	5.8	6.61
Malavangatta aged clay	–	–	5.0	6.6	32.0	5.3	–	8.8	50.0	5.82	–
Ranchi H-clay	48.65	16 6	4.27	7.4	36.0	5.75	9.4	8.75	60.0	6.85	7.52
Ranchi aged clay	–	–	5.0	6.6	24.0	5.8	–	8.35	38.5	6.3	–
Nainital H-clay	13.93	16.0	4.37	8.65	11.0	6.15	7.66	11.5	20.0	7.6	3.68
Nainital aged clay	–	–	6.1	8.6	8.0	6.7	–	9.75	17.5	8.7	–
Kulu H-clay	15.28	12.0	3.8	8.45	13.5	6.55	7.94	9.6	23.0	7.5	6.34
Kulu aged clay	–	–	5.15	7.9	12.0	6.7	–	9.5	22.5	7.65	–

TABLE 3—PYRIDINE TITRATION DATA

Clay samples	B. E. C. meq/100 g	Initial pH value (0.6% suspension)	At inflexion point		pK value
			pH	meq pyridine/100 g H-clay	
Bagespura H-Clay	78.0	3.1	5.27	24.0	4.95
Bagespura aged clay	–	4.05	5.6	19.5	5.12
Malavangatta H-clay	49.92	3.37	4.9	25 0	4.35
Malavangatta aged clay	–	5.0	5.3	20.0	4.85
Ranchi H-clay	48.65	4.27	5.23	25.0	5.06
Ranchi aged clay	–	5.0	5.45	20.0	5.3
Nainital H-clay	13.93	4.37	6.0	20.0	5.7
Nainital aged clay	–	6.1	6.45	18.0	6.33
Kulu H-clay	15.28	3.8	6.15	24.0	5.9
Kulu aged clay	–	5.15	6.25	18.0	6.0

clays can be determined. pK_1 values from pyridine titrations are lower than that from alkali titrations. This shows that stronger alkali can neutralise some hydroxy Al species along with active acidity and shows higher inflexion points. On ageing, pyridine titrations show lower inflexion points due to loss of active acidity from the exchangeable sites similar to that of alkali titrations. An interesting feature is that the adsorption of pyridine on acid chlorites is higher than that of acid vermiculites, inspite of the fact that vermiculites are expanding lattice minerals and possess organophillic character. It is considered as due to part of pyridine adsorption on acid chlorites is made by Van der waal's forces.

References

1. C. E. MARSHALL, "The Colloid Chemistry of Silicate Minerals", Academic Press, New York, 1949.
2. R. E. GRIM, "Clay Mineralogy", McGraw-Hill, New York, 1968.
3. R. P. MITRA and B. S. KAPOOR, *Soil Sci.*, 1969, **108**, 11.
4. M. L. JACKSON, *Soil Sci. Soc. Am. Proc.*, 1963, **27**, 10.
5. U. SCHWERTMANN and M. L. JACKSON, *Soil Sci. Soc. Am. Proc.*, 1964, **28**, 179.
6. N. T. COLEMAN and G. W. THOMAS, *Soil Sci. Soc. Am. Proc.*, 1964, **28**, 187.
7. M. ADHIKARI and M. K. MAJUMDAR, *Trans. Indian Ceram. Soc.*, 1973, **32**, 6, 129.
8. S. KHAN and J. P. SINGHAL, *J. Indian Chem. Soc.*, 1960, **45**, 4, 317.
9. C. S. PIPER, "Soil and Plant Analysis", Interscience, New York, 1950.
10. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longmans Green, London, 1969.
11. M. ADHIKARI, M. K. MAJUMDAR and A. K. PATI, *Trans. Indian Ceram. Soc.*, 1982, **41**, 78.

J. Indian Chem. Soc.
Vol. LXI, October 1984, pp. 876-879

Mechanistic Study of Oxidation of Secondary Alcohols by *N*-Bromosaccharin in Presence of Saccharin

K. VIJAYA MOHAN, P. RAGHUNATH RAO and E. V. SUNDARAM*

Department of Chemistry, University College, Kakatiya University, Warangal-506 009

Manuscript received 1 October 1983, revised 22 August 1984, accepted 20 September 1984

Oxidation of secondary alcohols including cyclic alcohols by NBSacc has been carried out in presence of added saccharin (reduction product of NBSacc) and Hg^{II} ions. The behaviour of substrates is anomalous, but irrespective of substrate the oxidant exhibits first order. Addition of acid catalyses the reaction and variable order in $[H^+]$ has been noticed. Among the 2-ols studied the order of reactivity observed is propanol < butanol < pentanol < octanol, and with cyclic alcohols the order is cyclopentanol < cycloheptanol < cyclooctanol. There is marginal decrease in rate with increasing percentage of acetic acid and increasing concentration of Na_2SO_4. Corresponding ketone is reported to be the product of oxidation. The activation parameters have been calculated and the mechanistic conclusions are discussed.

ALTHOUGH NBSacc has been used in the preparative organic chemistry as oxidising and halogenating reagent[1], the mechanism of its oxidation of alcohols has not yet been established. However, its analogues *N*-bromosuccinimide[2], *N*-chlorosuccinimide[3] and *N*-bromoacetamide[4] have received substantial attention and several studies on the mechanism of their reaction have been reported in recent years. The different mechanistic pathways reported for these structurally related compounds prompted us to undertake this investigation. We report in this communication the results of rate measurements on the NBSacc oxidation of secondary alcohols including cyclic alcohols in aqueous acetic acid medium in the presence of saccharin. The mechanistic conclusions are also discussed.

Experimental

All the chemicals used were of A.R. grade and purified further either by recrystallisation or by distillation - acetic acid, butan-2-ol and pentan-2-ol (A.R, B.D.H.) cyclopentanol and cycloheptanol A.G., Fluka, cyclooctanol (Koch-Light), propan-2-ol and octan-2-ol (E. Merck). Acetic acid was refluxed over chromium trioxide. The middle fraction boiling at 117-118° (lit. 118.5°) was used. The oxidant was prepared by the bromination of saccharin by usual procedure[1].

The reactions were carried out in 60% (v/v) acetic acid-water mixture in the presence of 0.004 *M* $Hg(OAc)_2$ and 0.02 *M* saccharin at desired sulphuric acid concentration in the temperature range of 10-50°. During the oxidation of alcohols by NBSacc in acid medium, bromide and bromine are liberated *in situ*, which can be explained by the equations (1) and (2).

$$\begin{matrix}R\\R'\end{matrix}\!\!>CH-O-H+C_7H_4SO_3N\text{-}Br \longrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>C=O+Br^-+C_7H_4SO_3NH+H^+ \quad (1)$$

$$NBSacc+Br^- \overset{H^+}{\rightleftharpoons} Saccharin+Br_2 \quad (2)$$

The liberated bromine may also oxidize alcohols. Hence, formation of Br_2 is suppressed by the addition of mercuric acetate[5] which traps Br^- and forms an unionised $HgBr_2$ or $HgBr_4^{2-}$. It was observed that the pseudo-first order plots without added saccharin showed considerable departure from linearity after 20% of the reaction. This was attributed to the retarding effect of saccharin. However, with added saccharin the deviation from linearity disappeared and at the same time the rates were diminished. Therefore, we carried out all the reactions in the presence of added saccharin.

The kinetics of the reaction were followed by estimating unreacted oxidant iodometrically. All the experiments were carried out under pseudo-first order conditions using ten-fold excess of [substrates] over the [oxidant] and in the presence of saccharin. The stoichiometry of the reaction was determined by keeping the excess oxidant concentration over substrates and estimating the unreacted oxidant concentration from time to time.

Results and Discussion

The stoichiometry of the reaction was found to be one mole of alcohol to one mole of oxidant as given by the equation (1). The products obtained were corresponding ketones which were identified by preparing the corresponding 2,4-DNP derivatives and comparing their melting points with the literature values[6]. Bromide ions were identified by th

TABLE 1—EFFECT OF [SUBSTRATE] ON OBSERVED RATE CONSTANTS IN OXIDATION OF SECONDARY ALCOHOLS BY NBSACC

[NBSacc] = 0.002 *M*, $[Hg(OAc)_2]$ = 0.004 *M*, Aq. HOAc = 60% (v/v), Temp. = 45°
$[H_2SO_4]$ = 0.50 *M*, [saccharin] = 0.02 *M*

Alcohol	$k_{obs}\times10^5$ s^{-1} at [substrate] × 10^2 *M*							
	1.0	2.0	2.5	4.0	5.0	6.0	10.0	20.0
Propan-2-ol	2.72	4.62	5.82	8.01	9.36	11.0	15.4	28.4
Butan-2-ol	–	–	9.11	13.2	15.5	17.8	27.0	47.8
Pentan-2-ol	3.80	7.32	8.72	13.0	16.3	19.2	28.4	54.8
Octan-2-ol	–	9.53	11.9	20.4	26.5	32.4	54.8	127
Cyclopentanol*	4.41	9.97	13.5	22.6	29.2	35.7	–	–
Cycloheptanol*	14.8	30.7	–	56.8	–	101	–	–
Cyclooctanol*	24.8	51.2	64.6	97.6	133	–	–	–

*$[H_2SO_4]$ = 0.05 *M*.

usual test. When acrylonitrile was added to the reaction mixture no polymerization was observed indicating that the reaction did not involve free radicals.

The order with respect to oxidant was found to be unity. The pseudo-first order rate constants increased with increasing alcohol concentration (Table 1). Plots of log k_{obs} *vs* log [substrate] are linear for all the alcohols studied, but slopes are not equal. Slopes are unity in the case of pentan-2-ol, octan-2-ol and all the cyclanols studied, whereas less than unity in the case of propan-2-ol and butan-2-ol. The order with respect to [saccharin] is fractional negative order (Table 2),

TABLE 2—EFFECT OF [SACCHARIN] ON OBSERVED RATE CONSTANTS IN OXIDATION OF SECONDARY ALCOHOLS BY NBSACC

[NBSacc] = 0.002 *M*, $[Hg(OAc)_2]$ = 0.004 *M*,
Aq. HOAc = 60% (v/v), Temp. = 45°

Alcohol	$k_{obs}\times10^4$ s^{-1} at [saccharin] × 10^2 *M*				
	1.0	2.0	3.0	4.0	5.0
Butan-2-ol*	2.33	1.83	1.46	1.32	1.22
Octan-2-ol*	3.34	2.65	2.35	2.13	1.89
Cycloheptanol**	3.65	3.07	2.26	2.02	1.97
Cyclooctanol**	8.34	5.11	5.11	4.26	–

*[substrate] = 0.05 *M*, $[H_2SO_4]$ = 0.50 *M*.
**[substrate] = 0.02 *M*, $[H_2SO_4]$ = 0.05 *M*.

which is confirmed from the linear plots of log k_{obs} *vs* log [saccharin]. The rate of oxidation was also enhanced with increase in sulphuric acid concentration, thus exhibiting acid catalysis. The dependence of rate on $[H^+]$ is found to be fractional from the linear plots of log k_{obs} *vs* log $[H^+]$. The reactions were studied in the temperature range of 30 to 50°. The observed rate constants and activation parameters are recorded in Table 3. *N*-Bromosaccharin like other similar *N*-halo-compounds may exist in various forms in acid medium[4,7], namely free *N*-bromosaccharin, protonated *N*-bromosaccharin or Br^+, and it can also exist as HOBr or $H_2\overset{+}{O}Br$ in acid medium. The different forms of reactive species for oxidant can be

TABLE 3—ORDER OF REACTIVITY AND ACTIVATION PARAMETERS IN OXIDATION OF SECONDARY ALCOHOLS BY NBSACC

[NBSacc] = 0.002 *M*, Aq. HOAc = 50% (v/v),
$[Hg(OAc)_2]$ = 0.004 *M*, [saccharin] = 0.02 *M*

Sl. no.	Substrate	$k_{obs}\times10^5$ sec^{-1} at 35°	$\Delta H^{\ne}$ JK mol^{-1}	$-\Delta S^{\ne}$ JK mol^{-1}	$\Delta G^{\ne}$ kJ mol^{-1}
1.	Propan-2-ol	3.43	69.3	105	102
2.	Butan-2-ol	6.85	69.3	99	99.9
3.	Pentan-2-ol	7.38	77.3	74	96.4
4.	Octan-2-ol	10.5	82.6	54	99.0
5.	Cyclopentanol	3.20	86.5	50	102
6.	Cycloheptanol	12.0	66.6	101	97.6
7.	Cyclooctanol	25.6	71.7	81	96.9

Sl. nos. : 1-4 [Substrate] = 0.05 *M*, $[H_2SO_4]$ = 0.50 *M*,
5-7 [Substrate] = 0.02 *M*, $[H_2SO_4]$ = 0.05 *M*.

represented by the following equilibrium.

$$\text{NBSacc}+H^+ \rightleftharpoons \text{Saccharin}+Br^+ \quad (3)$$

$$\text{NBSacc}+H^+ \rightleftharpoons \text{NBSacc } H^+ \quad (4)$$

$$\text{NBSacc}+H_2O \rightleftharpoons \text{HOBr}+\text{Saccharin} \quad (5)$$

$$\text{HOBr}+H^+ \rightleftharpoons H_2\overset{+}{O}Br \quad (6)$$

If free NBSacc is active species, there will not be any effect of saccharin on the rate of reaction. But our results show that saccharin inhibits the rate indicating that free NBSacc is not reactive species. If Br^+, HOBr, and $H_2\overset{+}{O}Br$ are the active species the oxidation rate will be diminished by added saccharin which was observed in the present work. However, if Br^+ and $H_2\overset{+}{O}Br$ are the active species the reaction should show acid catalysis. Our observations show that there is no acid catalysis in the absence of added saccharin, thus eliminating the possibility of Br^+ or $H_2\overset{+}{O}Br$ being the active species. In the presence of added saccharin the oxidation process exhibits acid catalysis and is inhibited by saccharin, with fractional order dependence of rate with respect to $[H^+]$ as well as [saccharin]. In presence of added saccharin equilibrium (5) may be shifted towards left thus the formation of the protonated NBSacc may become important.

Taking all these facts into consideration protonated form of the oxidant along with HOBr are proposed as active forms of oxidant participating in the oxidation process. Therefore, in the presence of added saccharin and in sulphuric acid medium, we suggest the following mechanism in which the alcohol attacks the active species of oxidant in rate determining step.

$$\text{NBSacc} + \text{H}^+ \xrightleftharpoons{K_1} \text{NBSacc H}^+$$

$$\text{NBSacc H}^+ + \text{alcohol} \xrightarrow[\text{slow}]{k'_1} \text{products}$$

$$\text{NBSacc} + \text{H}_2\text{O} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{HOBr} + \text{Saccharin}$$

$$\text{HOBr} + \text{alcohol} \xrightarrow[\text{slow}]{k_3} \text{products}$$

Based on this mechanism the following rate expression can be obtained,

$$-\frac{d}{dt}[\text{NBSacc}] = K_1k'_1[\text{NBSacc}][\text{H}^+][\text{alcohol}] + \frac{k_1k_3[\text{NBSacc}][\text{alcohol}]}{k_2[\text{saccharin}] + k_3[\text{alcohol}]}$$

which explains fractional order dependence on [alcohol] and [H$^+$] and inhibition by saccharin, while under the conditions of k_2 [saccharin] >> k_3 [alcohol], a first order dependence on [alcohol] which is observed in case of pentan-2-ol, octan-2-ol and cyclic alcohols.

An attempt has been made to evaluate the rate constants $K_1k'_1$ and k_1k_3/k_2 by studying the reactions at various concentrations of alcohol and H_2SO_4 (Table 4). Under the conditions k_2 [Sacc] >> k_3 [alcohol], a plot of k_{obs} *vs* [H$^+$] gives a straight line with a slope equal to $K_1k'_1$ [alcohol] and intercept equal to (k_1k_3/k_2) [alcohol]/[saccharin]. A plot of slope *vs* [alcohol] and a plot of intercept *vs* ([alcohol]/[saccharin]) give straight lines passing through the origin with slopes to $K_1k'_1$ and k_1k_3/k_2, respectively. As an example for octan-2-ol, the value of $K_1k'_1$ is equal to $0.635 \times 10^{-2} l^2 m^{-2} s^{-1}$ while k_1k_3/k_2 is equal to $37 \times 10^{-6} s^{-1}$. It has been observed that the oxidation of cyclic alcohols is faster than that of 2-ols. The observed rate constants (k_{obs}), $K_1k'_1$ and k_1k_3/k_2 values for cyclooctanol and octan-2-ol are given in Table 5. A perusal of rate data shows that cyclic alcohols react ten times faster than 2-ols. The $K_1k'_1$ and k_1k_3/k_2 values are also in accordance with rate data for both the alcohols. The $K_1k'_1$ and k_1k_3/k_2 values are proportional to k'_1 and k_3, respectively as K_1 and k_1/k_2 are the equilibrium constants and independent of the nature of alcohol. The ratio of $k'_{1(cyclic\ alcohol)}/k'_{1(2-ol)}$ and $k_{3(cyclic\ alcohol)}/k_{3(2-ol)}$ are 11 and 10 times, respectively which agree with our experimental results.

TABLE 4—EFFECT OF [OCTAN-2-OL] ON OBSERVED RATE CONSTANTS AT VARIOUS [H_2SO_4]

[NBSacc] = 0.002 *M*, [saccharin] = 0.02 *M*, [Hg(OAc)$_2$] = 0.004 *M*, Aq. HOAc = 60% (v/v), Temp. = 45°

[Octan-2-ol]	$k_{obs} \times 10^4$ s^{-1} at [H_2SO_4]			
	0.1	0.2	0.5	0.8
0.025	0.78	1.01	1.19	1.92
0.05	2.02	2.13	2.65	4.04
0.10	2.95	3.75	5.48	9.50
0.20	5.82	7.68	12.8	21.3
0.25	7.99	9.59	19.2	29.6

TABLE 5—OBSERVED RATE CONSTANTS (k_{obs}), $K_1k'_1$ AND k_1k_3/k_2 VALUES FOR ALCOHOLS

[NBSacc] = 0.002 *M*, Aq. HOAc = 60% (v/v), [Hg(OAc)$_2$] = 0.004 *M*, [saccharin] = 0.02 *M*, [substrate] = 0.02 *M*, [H_2SO_4] = 0.1 *M*, Temp. = 45°

Substrate	k_{obs} $\times 10^4$ s^{-1}	$K_1k'_1$ $\times 10^2 l^2 m^{-2} s^{-1}$	k_1k_3/k_2 $\times 10^4$ sec^{-1}
Cyclooctanol	7.6	8.00	3.98
Octan-2-ol	0.76	0.64	0.37

The data given in Table 3, show that under similar experimental conditions the order of reactivity is propan-2-ol <butan-2-ol< pentan-2-ol <octan-2-ol. Rate of oxidation increases with the increase of length of carbon chain. As the chain length increases the +I effect increases resulting in the enhancement of electron density at the hydroxyl bearing carbon atom.

The order of reactivity for three cyclanols studied is cyclopentanol <cycloheptanol <cyclooctanol. The rate is increasing with increasing ring size. Similar order of reactivity is observed in the oxidation of cyclanols by acid bromate[8,9], bromine[10-12] and NBS[2].

Acknowledgement

One of the authors (K. V. M.) wishes to thank C. S. I. R., New Delhi for the award of Junior Research Fellowship.

References

1. J. N. BACHHAWAT and N. K. MATHUR, *Indian J. Chem.*, 1971, **9**, 1335.
2. V. THIAGARAJAN and N. VENKATASUBRAMANIAN, *Indian J. Chem.*, 1970, **8**, 809.
3. N. S. SRINIVASAN and N. VENKATASUBRAMANIAN, *Tetrahedron*, 1974, **30**, 419.

4. J. MUKHERJEE and K. K. BANERJI, *J. Org. Chem.*, 1981, **46**, 323.

5. J. C. BAILAR, "The Chemistry of Coordination Compounds", Reinhold, New York, 1956, p. 4.

6. A. I. VOGEL, "A Text Book of Practical Organic Chemistry", 3rd. ed., Longmans Green, London, 1961, p. 346.

7. E. BISHOP and V. J. JENNINGS, *Talanta*, 1958, 197.

8. V. LAKSHMI and E. V. SUNDARAM, *J. Indian Chem. Soc.*, 1980, **57**, 800.

9. V. LAKSHMI and E. V. SUNDARAM, *J. Indian Chem. Soc.*, 1978, **55**, 567.

10. V. THIAGARAJAN and N. VENKATASUBRAMANIAN, *Indian J. Chem.*, 1969, **7**, 830.

11. K. K. BANERJI, *Indian J. Chem.*, 1973, **11**, 244.

12. V. THIAGARAJAN and N. VENKATASUBRAMANIAN, *Indian J. Chem.*, 1970, **8**, 149.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 880-882

Hydration-Annealing of Chemical Radiation Damage in Calcium Nitrate

S. M. K. NAIR* and C. JAMES

Department of Chemistry, University of Calicut, Kerala-673 635

Manuscript received 25 October 1983, revised 10 May 1984, accepted 15 August 1984

The effect of hydration on the annealing of chemical radiation damage in anhydrous calcium nitrate has been investigated. Rehydration of the anhydrous irradiated nitrate induces direct recovery of the damage. The rehydrated salt is susceptible to thermal annealing but the extent of annealing is small compared to that in the anhydrous salt. The direct recovery of damage on rehydration is due to enhanced lattice mobility. The recovery process is unimolecular.

A considerable amount of work has been done on the thermal annealing of chemical radiation damage in ionic nitrates and the influence of various factors thereon[1-4]. It has been observed that phase transformations in irradiated crystals induce rapid recombination of damage fragments and the recombination virtually ceases once the phase transformation has taken place[5-7]. The effect of lattice rearrangement accompanying loss of water of crystallisation on the annealing of chemical radiation damage in calcium bromate monohydrate-anhydrous system has also been reported[8]. However, published information on the effect of post irradiation hydration on the annealing of chemical radiation damage is not available. It was of interest, therefore, to investigate the effect of regain of water of crystallisation on the annealing of chemical radiation damage in anhydrous salts. Ionic nitrate, such as calcium nitrate has been chosen for this investigation because it is formed as crystalline nitrate with water of crystallisation and the regain of water by the anhydrous nitrate to form the tetrahydrate takes place at room temperature. Moreover, the kinetics of thermal annealing of chemical radiation damage in this system has been investigated in detail[9]. A preliminary note on the effect of hydration on the annealing of chemical radiation damage in cadmium nitrate has already appeared[10].

Experimental

Calcium nitrate tetrahydrate (A. R. grade) was dehydrated to constant weight at 170° in a thermostated electric hot air oven and stored over phosphorus pentoxide in a vacuum desiccator. Portions of the anhydrous salt sealed *in vacuo* in pyrex glass ampoules were irradiated at room temperature with ^{60}Co γ-rays to a dose of 52 Mrad at a dose rate of 0.2 Mrad h^{-1}. The irradiated samples were preserved over phosphorus pentoxide in vacuum desiccator. Due to the highly hygroscopic nature of the anhydrous salt it was always handled in a dry box.

The damage nitrite was estimated spectrophotometrically with a Beckman DU2 instrument by Shinn[11] method as modified by Kershaw and Chamberlin[12] to an accuracy of $\pm 1\%$.

The effect of regain of water of crystallisation on the initial nitrite content in γ-irradiated anhydrous calcium nitrate was studied by keeping known weights of the irradiated sample in a constant humidity controlled atmosphere[13] of relative humidity 93.9% for various time intervals, from 0-265 h at room temperature and estimating the NO_2^- content at the end of each time interval. The weight of the irradiated salt at the end of the above time interval agreed with the uptake of four molecules of water of crystallisation indicating complete rehydration.

Isothermal annealing runs were made in air in glass tubes in a thermostated electric hot air oven maintained to within $\pm 1°$ of the desired temperature, with samples of the irradiated anhydrous salt, the irradiated sample rehydrated at room temperature and also with the sample desiccated after rehydration.

Results and Discussion

The damage induced by 52 Mrad ^{60}Co γ-rays in anhydrous calcium nitrate was 4058 p.p.m. of NO_2^-. There was progressive diminution of NO_2^- content during rehydration. Typical plots of nitrite concentration *vs* time of rehydration are given in Fig. 1. The plots are linear which implies an unimolecular recombination process. The velocity constant is $3.84 \times 10^{-4} h^{-1}$.

The thermal annealing characteristic of irradiated anhydrous calcium nitrate at 300° along with those of the rehydrated sample and the sample desiccated after rehydration are shown in Fig. 2. The regain of water of crystallisation by the irradiated anhydrous

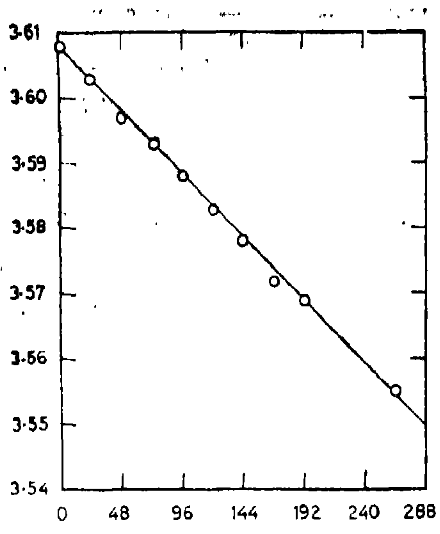


Fig. 1. Annealing of chemical radiation damage in anhydrous calcium nitrate on rehydration.

appreciable energy of activation and that the energy input to the system is only utilised for the release and migration of the damage oxygen. The annealing on rehydration of the anhydrous salt and subsequent thermal annealing of the rehydrated salt can therefore be explained as follows. The rehydration of the anhydrous salt results in phase change. The lattice mobility during the phase change liberates the damage oxygen and a proportion of these combine with nitrite to give nitrate ions. This results in the annealing observed on rehydration. However, a small portion of the fragments could survive the lattice rearrangement[16]. These fragments anneal back to nitrate on heating. Since the proportion of these fragments is small the extent of thermal annealing after rehydration is very small as observed.

The thermal annealing of chemical radiation damage in ionic nitrates is a combination of a first order process, which corresponds to the recombination of close correlated nitrite ion-oxygen atom pairs, and a second order process involving random

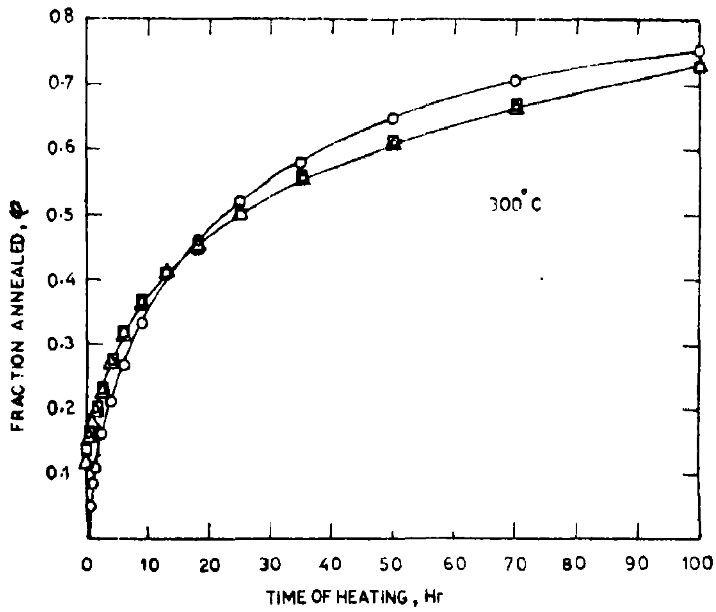


Fig. 2. Effect of rehydration and subsequent desiccation on thermal annealing of chemical radiation damage in calcium nitrate, (O) irradiated anhydrous salt, (△) irradiated anhydrous salt rehydrated, (□) irradiated anhydrous salt desiccated after rehydration.

nitrate at room temperature to form the tetrahydrate results in the recovery of damage, to the extent of ϕ=0.116, where ϕ is the fraction annealed[14]. The subsequent thermal annealing behaviour of the rehydrated salt is quite normal although the extent of annealing is smaller than that for the irradiated anhydrous salt. Desiccation of the rehydrated salt produces an additional recovery of ϕ=0.02. The thermal annealing behaviour of the sample desiccated after rehydration is also similar to that of the rehydrated sample.

In the model of annealing developed by Maddock and Mohanty[1,15] it has been proposed that the recombination of the damage fragments (NO_2^- and O in the case of nitrates) occurs without recombination of the damage fragments throughout the crystal[17]. The percentage of NO_2^- that recombine by the first order mechanism in irradiated calcium nitrate is 12 and the corresponding energy of activation is 16.9 kcal mol^{-1}. The extent of hydration annealing is smaller in the case of calcium nitrate compared to that in cadmium nitrate[10]. This low magnitude of annealing is due to the small percentage of the primary fragments and the higher energy of activation involved.

Acknowledgement

Grateful thanks of the authors are due to M/s Western India Plywoods, Baliapattam, Kerala for irradiations.

References

1. A. G. MADDOCK and S. R. MOHANTY, *Discuss. Faraday Soc.*, 1961, **31**, 193.
2. E. CHANDUNNI and S. M. K. NAIR, *Rad. Eff. Lett.*, 1981, **58**, 5.
3. E. CHANDDUNI, Ph. D. Thesis, University of Calicut, 1981.
4. M. S. KRISHNAN, Ph. D. Thesis, University of Calicut, 1981.
5. A. G. MADDOCK and S. R. MOHANTY, *Radiochim. Acta*, 1963, **1**, 85.
6. S. R. MOHANTY and S. R. UPADHYAY, *Indian J. Chem.*, 1965, **3**, 285.
7. E. CHANDUNNI and S. M. K. NAIR, *Radiochim. Acta*, 1979, **26**, 177.
   M. KHARE and S. R. MOHANTY, *J. Inorg. Nucl. Chem.*, 1967, **29**, 853.
9. S. M. K. NAIR, C. JAMES and C. S. PEARLY, *Radiochim. Acta*, 1983, **32**, 202.
10. S. M. K. NAIR and C. JAMES, *Indian J. Chem., Sect. A*, 1982, **21**, 504.
11. M. B. SHINN, *Ind. Engg. Chem., Anal. Ed.*, 1941, **13**, 83.
12. N. F. KERSHAW and N. S. CHAMBERLIN, *Ind. Engg. Chem., Anal. Ed.*, 1942, **14**, 312.
13. E. CHANDUNNI, M. S. KRISHNAN and S. M. K. NAIR, *J. Indian Chem Soc.*, 1978, **55**, 574.
14. M. S. KRISHNAN and S. M. K. NAIR, *J. Indian Chem. Soc.*, 1979, **56**, 805.
15. S. R. MOHANTY and S. R. UPADHYAY, *Z. Phys. Chem.*, 1968, **57**, 3.
16. J. R. BOLTON and K. J. MCCALLUM, *Can. J. Chem.*, 1957, **35**, 761.
17. S. M. K. NAIR, M. S. KRISHNAN and C. JAMES, *Rad. Eff.*, 1983, **71**, 87.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 883-884

Synthesis of 2-Phenylimino-3-aryl/*H*-4-*S*-benzyl-6-tetra-*O*-acetyl-D-glucopyranosylimino-2,3-dihydro-1,3,5-thiadiazines

B. N. BERAD, S. P. DESHMUKH and M. G. PARANJPE*

Department of Chemistry, Nagpur University, Nagpur-440 010

Manuscript received 18 January 1984, accepted 30 May 1984

2-Phenylimino-3-aryl/*H*-4-*S*-benzyl-6-tetra-*O*-acetyl-D-glucopyranosylimino-2, 3-dihydro-1,3,5-thiadiazine hydrochlorides (IIIa-IIIf) have been synthesized directly by the interaction of phenyl isocyanodichloride (I) and 1-aryl/*H*-5-tetra-*O*-acetyl-D-glucopyranosyl-2-*S*-benzyl-2,4-isodithiobiurets (IIa-IIf). Their structures have been supported on the basis of usual chemical transformations and ir spectral data. These could not be isomerised into corresponding 1,3,5-triazines.

RECENTLY, we have prepared 1-aryl/*H*-5-tetra-*O*-acetyl-D-glucopyranosyl-2-*S*-benzyl-2,4-isodithiobiurets (II) by the interaction of 1-aryl/*H*-*S*-benzylisothiocarbamide and tetra-*O*-acetyl-D-glucopyranosylisothiocyanate[1]. In view of our interest in *N*-glucosylated compounds, we now report the synthesis of 2-phenylimino-3-aryl/*H*-4-*S*-benzyl-6-tetra-*O*-acetyl-D-glucopyranosylimino-2,3-dihydro-1,3,5-thiadiazines.

The reaction of phenylisocyanodichloride[2] (I) and 1-phenyl-5-tetra-*O*-acetyl-D-glucopyranosyl-2-*S*-benzyl-2, 4-isodithiobiuret (IIa) in boiling benzene medium afforded a clear yellow solution. On distilling out benzene a syrupy mass was left. This on repeated triturations with petroleum ether gave a pale yellow solid, m.p. 110° (d). It was found unstable and on standing gradually decomposed into a sticky material. The product was found desulphurisable when boiled with alkaline plumbite solution. The product was acidic to litmus and gave effervescence with aqueous sodium bicarbonate solution. It gave a picrate m.p. 172°. The product has $[\alpha]_D^{31}$ −26.99° (c 0.4 in $CHCl_3$); ν_{max} 1750, (C=O), 685 (C−S), 1595 (S−C=N), and 1580 cm^{-1} (N−C=N) bands[3,4]. Bands due to the isotriazine ring structure at 1550 and 750 cm^{-1} were missing. Therefore, the product has been assigned the structure 2-phenylimino-3-phenyl-4-*S*-benzyl-6-tetra-*O*-acetyl-D-glucopyranosylimino-2,3-dihydro-1,3,5-thiadiazine hydrochloride (**IIIa**).

The reaction of phenylisocyanodichloride has been extended to other 1-aryl/*H*-5-tetra-*O*-acetyl-D-glucopyranosyl-2-*S*-benzyl-2,4-isodithiobiurets to obtain **IIIb** to **IIIf** (Table 1).

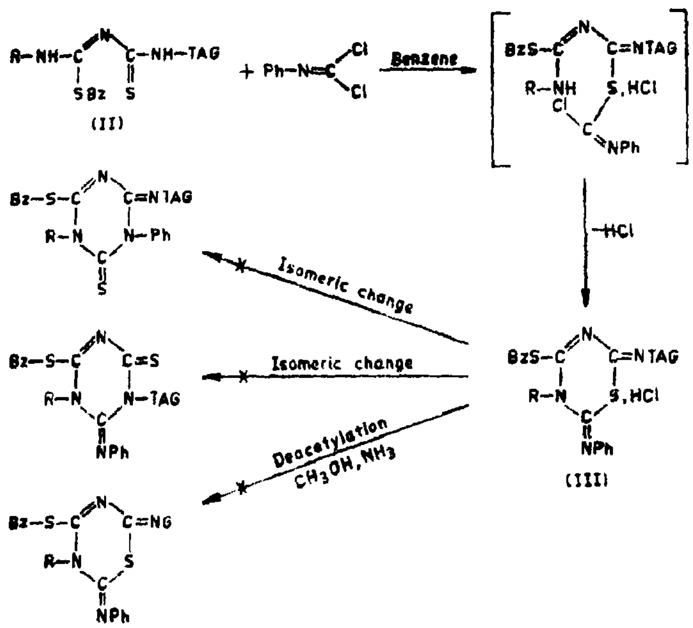
Isomerisation of these 1,3,5-thiadiazines (III) have been tried in several ways but without success. Also, these could not be deacetylated into the corresponding D-glucopyranosyl forms. when tried with methanolic ammonia.

TABLE 1—2-PHENYLIMINO-3-ARYL/*H*-4-*S*-BENZYL-6-TETRA-*O*-ACETYL-D-GLUCOPYRANOSYLIMINO-2,3-DIHYDRO-1,3,5-THIADIAZINE (HYDROCHLORIDE) (III)

1-Aryl/*H*-5-tetra-*O*-acetyl-D-glucopyranosyl-2-*S*-benzyl-2,4-isodithiobiurets used : 0.01 *M*.
N-Phenylisocyanodichloride used : 1.8 g

Sl. no.	Isodithiobiuret used (g)	1,3,5-Thiadiazine hydrochloride (III), yield (g)	Yield %	M.p. °C(d)	Analysis % : Found/(Calcd.) N	S	Eq. wt. Found/ (Calcd.)	$[\alpha]_D^{31}$ in $CHCl_3$ deg	Picrate M.p. °C	N% Found/ (Calcd.)
1.	1-Phenyl (6.3)	−3-phenyl . . (6.5), IIIa	80	110	7.28 (7.28)	8.32 (8.23)	761.4 (768.5)	−26.99 (c 0.40)	172	9.83 (10.19)
2.	1-*o*-Tolyl (6.5)	−3-o-tolyl . . (5.8), IIIb	71	78	6.59 (7.15)	7.77 (8.17)	772.8 (782.5)	−31.90 (c 0.40)	108	9.52 (10.05)
3.	1-*p*-tolyl (6.5)	−3-p-tolyl . . (6.0), IIIc	73	105	6.89 (7.15)	8.30 (8.17)	770.2 (782.5)	+18.40 (c 0.40)	120	9.67 (10.05)
4.	1-*o*-Cl-phenyl (6.6)	−3-*o*-Cl-phenyl . . (5.5), IIId	65	115	6.83 (6.97)	8.03) (7.97)	790.2 (803.0)	−28.31 (c 0.40)	95d	9.63 (9.84)
5.	1-*p*-Cl-phenyl (6.6)	−3-p-Cl-phenyl . . (5.8), IIIe	69	82	6.64 (6.97)	7.00 (7.97)	794.0 (803.0)	+56.25 (c 0.40)	151d	9.58 (9.84)
6.	1-Hydrogen (5.5)	−3-hydrogen . . (5.5), IIIf	87	132	7.62 (8.08)	9.31 (9.24)	680.0 (692.5)	−22.09 (c 0.40)	Not isolated	

The compounds gave satisfactory C and H analyses.



Where, R = phenyl, o-tolyl, p-tolyl, o-Cl-phenyl, p-Cl-phenyl, hydrogen.
TAG = Tetra-*O*-acetyl-D-glucopyranosyl,
Bz = Benzyl, G = D-glucopyranosyl.

Experimental

2-Phenylimino-3-aryl/H-4-S-benzyl-6-tetra-O-acetyl-D-glucopyranosylimino-2,3-dihydro-1,3,5-thiadiazine hydrochloride (**III**) : Details of a typical experiment (where aryl=phenyl) are as follows.

To a suspension of 1-phenyl-5-tetra-*O*-acetyl-D-glucopyranosyl-2-*S*-benzyl-2,4-isodithiobiuret (0.01 *M*, 6.3 g) in benzene (50 ml) was added phenylisocyanodichloride (0.01 *M*, 1.8 g) and the mixture refluxed for 4 h. The evolution of hydrogen chloride was noticed. Benzene was distilled off and a syrupy mass was left. The mass on repeated trituration with petroleum ether gave a pale yellow solid (6.5 g). The product was purified by precipitating it from its benzene solution with petroleum ether. m.p. 110°(d) (Found : C, 49.20 ; H, 4.62 ; N, 7.28 ; S, 8.32 ; Eq. wt., 761 4. $C_{36}H_{38}O_{9}N_{4}S_{2}$. HCl requires C, 49.22 ; H, 4.87 ; N, 7.28 ; S, 8.23% ; Eq. wt., 768.5). Its ethanolic solution on reaction with picric acid afforded a picrate crystallised from ethanol-water, m.p. 172° (Found : N, 9.83. $C_{42}H_{40}O_{16}N_{7}S_{2}$ requires N, 10.19%).

Acknowledgement

Two of the authors (S.P.D and B.N.B.) are grateful to U.G.C. and C.S.I.R., New Delhi for the award of Junior Research Fellowships, and to Prof. K. N. Munshi for facilities.

References

1. S. P. DESHMUKH, B. N. BERAD and M. G. PARANJPE, *J. Indian Chem. Soc.*, communicated.
2. G. M. DYSON and T. HARINGTON, *J. Chem. Soc.*, 1940, 191.
3. N B. COLTHUP, C. H. DALY and S. E. WIBERLEY, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1963, p. 215.
4. R. M. SILVERSTEIN and G. C. BASSLER, "Spectrometric Identification of Organic Compounds", John Wiley, New York, 1963.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 885-887

Pyrazine Condensations from Malononitrile

JOE V. D'SOUZA*

Department of Chemistry, Indian Institute of Technology, Madras-600 036

Manuscript received 26 April 1983, revised 23 April 1984, accepted 15 August 1984

Tetrasubstituted pyrazines and pyridinopyrazines are rare to find or obtain. This paper reports that they are obtained from malononitrile. They can be modified at will for use in medicine. Two reactions are proposed for obtaining the highly basic intermediate II which is highly reactive to yield pyrazines.

PYRAZINES now find increasing application in dye chemistry[1-3] and in medicinal chemistry[4,5]. Among diuretics, the pteridines and pyrazines (amilioride) have shown high natriuretic but little kaliuretic effect[6-11]. The products of this work have been tested unsuccessfully in diuresis and against diabetes. Tetrasubstitued pyrazines are rare but show excellent tridentate liganding properties.

Experimental

Preparation of 2-aza-1,1,3,3-tetracyanopropane (**II**) :

Method A : The method of Wallenfels[12] was used. 25 g malononitrile was converted to the oxime[88] (ν_{max} 3000, 2200, 1700 cm^{-1} ; δ (D_2O) 1.9 ppm DOH 4.9 ppm methylene). Oximinomalononitrile was converted to the tosylate[88] (yellow-pink powder, m.p. 118° ; ν_{max} 2240, 1580, 1300 cm^{-1}). The sodium salt of malononitrile was prepared with molecular sodium in benzene. After the reaction the method of separation was as outlined below.

Method B : 25 g malononitrile was converted to oximinomalononitrile[83] and taken in 300 ml dry benzene. To it was added 25 g malononitrile and the mixture heated on a water bath and 5 ml piperidine and 5 ml acetic acid were added with stirring. Water was removed with a Dean and Stark apparatus. After removal of 100 ml benzene, vacuum was applied and benzene completely removed. Separation of the product was done as outlined below.

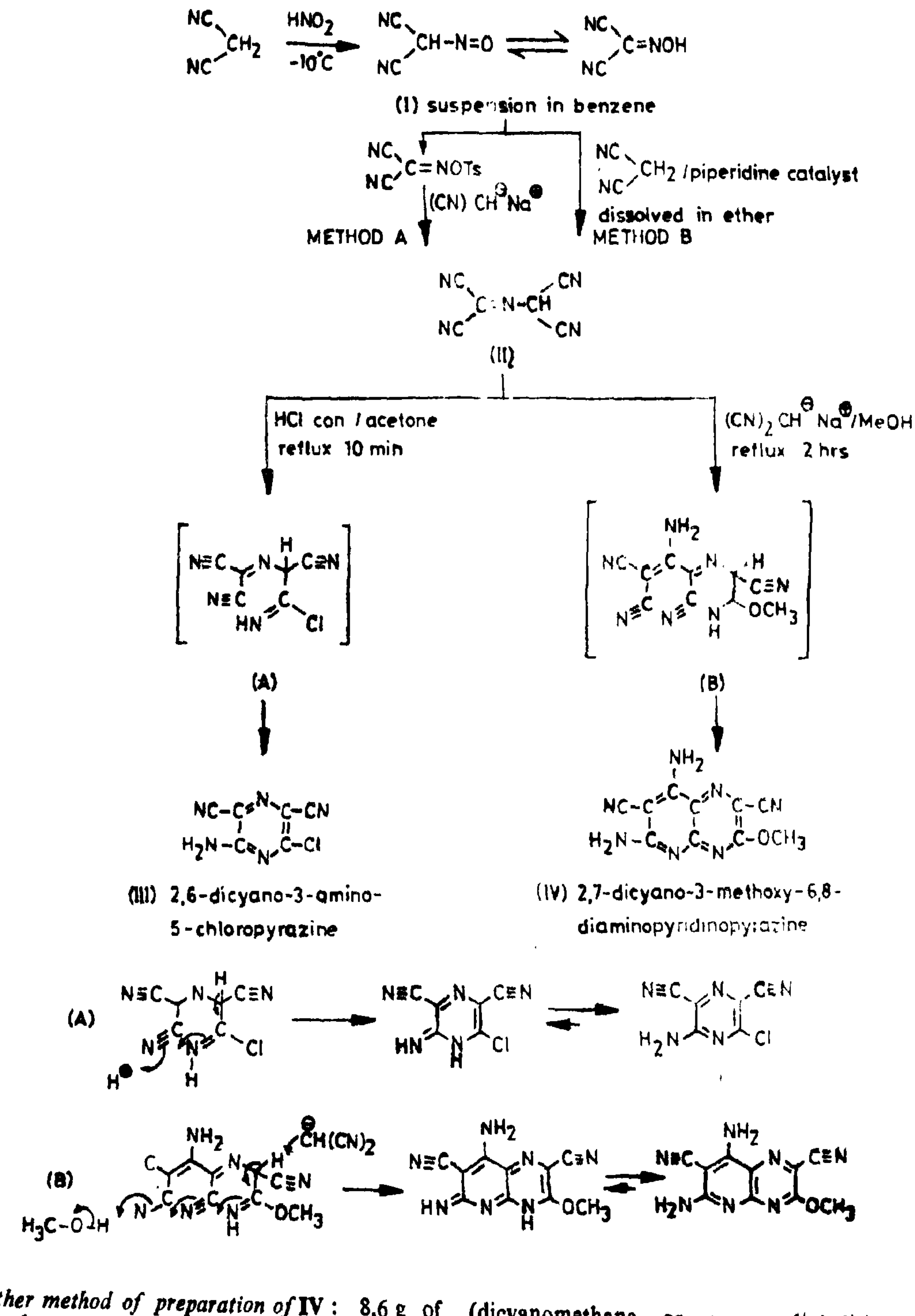
Separation of 2-aza-1,1,3,3-tetracyanopropane (**II**) : The residual thick brown product of Method A or B was chilled and treated with solid Na_2CO_3 till effervesence ceased. It was then extracted with 200 ml ether and the ether extract discarded. The residue was treated with a saturated acetone solution of 30 g mercuric chloride and the thick brown precipitate was filtered under vacuum and washed repeatedly with chilled acetone. A grey brown gel obtained was dried in a desiccator, m.p. >300° ; ν_{max} 1290 cm^{-1} (C–Hg–C).

The grey brown complex was taken in a three-necked round bottom flask connected with a funnel, stirrer and condenser with rubber tube exiting into a beaker of water. The flask was cooled in an ice bath and 30 g potassium cyanide in 200 ml acetone was added in aliquots. The ice-bath was removed and stirring continued for 1 h more. The flask was then connected to vacuum and acetone removed completely. The residue was extracted with 100 ml portions of ether five times and the combined ether extracts was dried under vacuum. The whole apparatus was then flushed with nitrogen and cooled. The bright yellow crystals separated were dried in a vacuum desiccator and recrystallised from methanol under nitrogen atmosphere, m.p. 98° ; ν_{max} 2210, 2200, 1480 cm^{-1}.

Preparation of 2,6-dicyano-3-amino-5-chloropyrazine (**III**) : 1.8 g of **II** was cyclised with HCl/acetone under reflux for 10 min[13]. The solution was chilled to obtain a precipitate. It was crystallised from ethanol to yield orange crystals decomposing after 3 days in air (45%) ; m.p. 245° (Found : C, 40.4 ; H, 0.94 ; N, 39 ; Cl, 19.6%) ; ν_{max} 3380, 3300, 2200, 1625 (NH_2), 2950, 1540 cm^{-1} (CN) ; aromatic n.m.r. in DMF or CF_3COOH shows no peak indicative of C-hydrogens ; *m/e* 179, 125, 152 and 144.

Preparation of 2,7-dicyano-3-methoxy-6,8 diamino-pyridino-pyrazine (**IV**) : 15 g of **II** was treated with 8.7 g sodium salt of malononitrile in 50 ml methanol and the mixture refluxed for 3 h. The flask was then chilled and the precipitate washed with methanol and ether. The crude was dissolved in DMF and reprecipitated with ether on cooling. The precipitate was filtered and dried to yield golden yellow crystals (70%), m.p. 312° (d) ; turned to red in 3 days ; soluble in acetic acid, DMF, DMSO and insoluble in ether, water ; ν_{max} 3400, 3300, 3340 (NH_2), 2200, 1625 (CN), 2950 cm^{-1} (aromatic) ; δ (DMF or CF_3COOH) 4.38 (OCH_3), 7.6 and 8.2 (N protons) when taken in CF_3COOH ; *m/e* 241, 210.

* Jesuit House, Panaji-403 001.



Another method of preparation of **IV** : 8.6 g of sodium salt of malononitrile in 30 ml methanol were treated with 20 g tosylate of oximinomalononitrile and refluxed for 3 h. The method of separation of IV was as given above ; overall yield, 55%.

Results and Discussion

According to the original method[12-17] of synthesis the sodium salt of malononitrile was reacted with nitrosotosylate of the same malononitrile (dicyanomethane or propanedinitrile) to give product II which can easily be cyclised. Another method that we have used for the first time in this reaction is the Knoevenagel reaction. This reaction is being increasingly made use of in malononitrile chemistry[18-19], and use of piperidine or Triton-B brought about high yields and eliminated many preparatory steps in the procedure. The use of phase transfer catalysts, TBAC or 18-crown-6 did not show any advantage over the use of piperidine.

Condensations are not uncommon in the chemistry of malononitrile[11-36] even though the starting material and products are often water sensitive. The substituents in the pyrazine system proved liable[20] and this admits of a variety of reactions on the products of our syntheses. The method of separation of II and the compound IV have not been reported earlier.

Ir and nmr data obtained by lagging the preparation of IV over 3 days at 0° indicate the formation of an imido-ester as an intermediate in the reaction. Spectral data also suggest the presence of iminotautomers in the final pyrazine products - the presence in each case of a strong band in the 1660 cm^{-1} region. The pyrazine absorptions can be assigned to 1580, 1550-30, 1470, 1380-50 cm^{-1}.

Materials : Malononitrile used was of B.D.H. or E. Merck. Ir spectra were recorded on a P. E. 257 spectrophotometer. Nmr spectra were recorded on a Varian XL 100 FT spectrometer. Mass spectra were recorded on a Varian Mat I.

Acknowledgement

The author is indebted to Farbwerke Hoechst A. G., the Department of Science and Technology and the Department of Chemistry, Indian Institute of Technology, Madras for financial support.

References

1. A. J. KLUYVER, J. P. VAN DER WALT and A. J. VAN TRIET, *Proc. Natl, Acad. Sci. U.S.A.*, 1953, 39, 583.
2. A. H. COOK and C. A. SLATER, *J. Chem. Soc.*, 1956, 4133.
3. J. C. MACDONALD, *Can. J. Chem.*, 1963, **41**, 165.
4. T. KOSUGE, H. KAMIYA and T. ADACHI, *J. Pharm. Soc., Jpn.*, 1964, **84**, 448.
5. R. GHIONE AND C. BERTAZZOLI, *Chem. Ber.*, 1909, **41**, 885.
6. G. JONES, H. F. RUSSO and A. ZACCHEI, *Fed. Proc.*, 1966, **25**, 197.
7. M. S. GLITZER and S. L. STEELMAN, *Nature (London)*, 1966, **212**, 191.
8. J. E. BAER, J. K. MICHAELSON, H. F. RUSSO and K. H. BEYER, *J. Pharmacol. Exp. Ther.*, 1966, **16**, 373.
9. A. ALBERT, D. J. BROWN and H. C. S. WOOD, *J. Chem. Soc.*, 1956, 2066.
10. J. CLARK, G. NEATH and C. SMITH, *J. Chem. Soc. C.*, 1969, 1297.
11. J. CLARK and C. SMITH, *J. Chem. Soc. C.*, 1971, 1948.
12. K. WALLENFELS, *Chimia*, 1966, **20**, 303.
13. K. FREDRICK, G. ERTEL and K. WALLENFELS, Ger Pat. 2 248 6601, 1974.
14. G. LONGO, *Gazz. Chim. Ital.*, 1931, **61**, 578, 561.
15. M. CONRAD and A. SCHULZE, *Chem. Ber.*, 1909, **42**, 735.
16. M. LOCQUIN and R. CERCHEZ, *Bull Soc. Chim. Fr.*, 1930, **47**, 1279.
17. J. PARCHAIS and J. P. FLEURY, *Tetrahedron*, 1972, **28**, 2267.
18. F. S. PROUT and V. D. BEUCAIRE, *J. Org. Chem.*, 1973, **38**, 1512.
19. J. M. BIEHLER, J. P. FLEURY, J. PARCHAIS and A. REGENT, *Tetrahedron Lett.*, 1968, **40**, 4227; *Bull. Soc. Chim.*, 1971, 2711.
20. M. WEISSENFELS and S. ILLING, *Z. Chem.*, 1973, **13**, 130.
21. E. L. LITTLE, W. J. MIDDLETON, D. D. COFFMAN, V. A. ENGELHARDT and G. N. SAUSEN, *J. Am. Chem. Soc.*, 1958, **80**, 2040.
22. W. J. MIDDLETON, E. L. LITTLE, D. D. COFFMAN and V. A. ENGELHARDT, *J. Am. Chem. Soc.*, 1958, **80**, 2795.
23. C. E. LOONEY and J R. DOWNING, *J. Am. Chem. Soc.*, 1958, **80**, 2840.
24. L. BIRKENBACH and K. HUTTNER, *Z. Anorg. Allg. Chem.*, 1930, **190**, 1.
25. E. ALLENSTEIN, *Chem. Ber.*, 1960, **101**, 1232; *Z. Anorg. Allg. Chem.*, 1961, **308**, 1.
26. B. C. MCKUSICK, R. E. HECKERT, T. L. CAIRNS, D. D. COFFMAN and H. F. MOWER, *J. Chem. Soc.*, 1958, **80**, 2805.
27. W. J. MIDDLETON, V. A. ENGELHARDT and B. S. FISCHER, *J. Am. Chem. Soc.*, 1950, **80**, 2822.
28. R. A. CARBONI, D. D. COFFMAN and E. G. HOWARD, *J. Am. Chem. Soc.*, 1958, **80**, 2838.
29. C. L. DICKINSON, D. W. WILEY and B. C. MCKUSICK, *J. Am. Chem. Soc.*, 1960, **82**, 6132.
30. R. E. MERRIFIELD and W. D. PHILLIES, *J. Am. Chem. Soc.*, 1958, **80**, 2889.
31. Zh. M. IVANOVA, N. A. KIRSANOVA, E. A. STUKALO and G. J. DERKACH, *J. Org. Chem. U.S.S.R.* (*Engl. Transl.*), 1967, 460.
32. G. KRESZE and E. ALBRECHT, *Chem. Ber.*, 1964, **97**, 490.
33. N. P. MARULLO and E. H. WAGNER, *J. Am. Chem. Soc.*, 1966, **88**, 5033.
34. J. A. FERRIS, R. A. SANCHEZ and L. E. MANCHUSO, *Org. Synth.*, 1968, **48**, 1.
35. K. FRIEDRICH and U. M. THIEME, *Chem. Ber.*, 1970, **103**, 1981.
36. K. FRIEDRICH and W. ERTEL, *Tetrahedron Lett.*, 1972, **47**, 4771.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 888-890

Condensed 1,8-Naphthyridines. Part-4. Synthesis of 7-Arylbenzimidazo[1′,2′:1,6]pyrimido[4,5-*b*] [1,8] naphthyridines

K. VIJAYENDER REDDY, K. MOGILAIAH and B. SREENIVASULU*

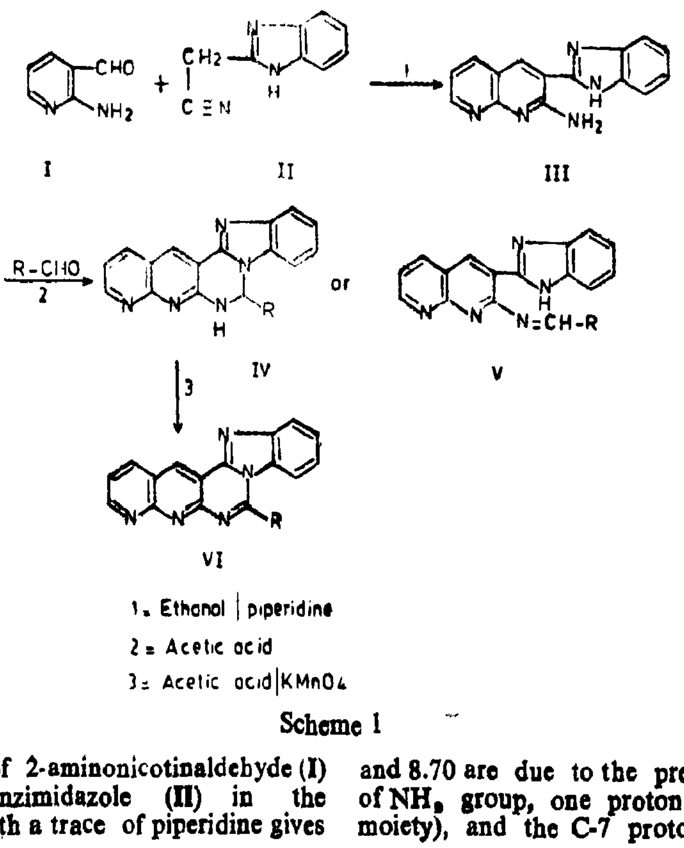
Department of Chemistry, University College, Kakatiya University, Warangal-506 009

Manuscript received 5 March 1984, accepted 15 August 1984

7-Arylbenzimidazo[1′,2′ : 1,6]pyrimido[4,5-*b*] [1,8]naphthyridines (VI) have been prepared by the oxidation of 7-aryl-6,7-dihydrobenzimidazo [1′,2′ : 1,6]pyrimido[4,5-*b*] [1,8]naphthyridines (IV). The dihydro compounds (IV) have been obtained by the condensation of benzaldehydes with 2-amino-3-(2-benzimidazolyl)-1,8-naphthyridine (III) which in turn obtained by the condensation of 2-aminonicotinaldehyde (I) with 2-cyanomethylbenzimidazole (II). The structures of the compounds have been established by elemental analyses and spectral data.

IN continuation of our earlier reports on the synthesis of 2-substituted[1-3] and 2,3-fused 1,8-naphthyridines[4-6], we describe in this paper the synthesis of hitherto unreported 7-arylbenzimidazo-[1′,2′ : 1,6] pyrimido [4,5-*b*] [1,8] naphthyridines. 1,8-Naphthyridines with heterocyclic system fused at 2,3-positions exihibit a variety of biological activities[7-14]. The synthetic approach to the title compounds is outlined in Scheme 1.

2-amino-3-(2-benzimidazolyl)-1,8-naphthyridine (III) in good yield. The structure assignment of III was based on its elemental analysis and ir, proton nmr and mass spectral data. The ir spectrum of III showed strong peaks at 3140 and 3420 cm^{-1} confirming the presence of benzimidazole-NH[15] and amino function on the 1,8-naphthyridine framework, respectively. In the proton nmr spectrum of III, ($DMSO-d_6+CDCl_3$) the signal at δ 2.45, 3.80



Scheme 1

The condensation of 2-aminonicotinaldehyde (I) with 2-cyanomethylbenzimidazole (II) in the presence of ethanol with a trace of piperidine gives

and 8.70 are due to the presence of two protons of NH_2 group, one proton of NH (benzimidazole moiety), and the C-7 proton on naphthyridine[16]

framework, respectively. The protons at C-4, C-5 and C-6 resonated along with four aromatic protons as a complex multiplet at 7.0-8.4. The mass spectrum of III showed strong peaks at m/z 261 (M^+, 100%), 260 (M^+-H, 26), 245 (M^+-NH_2, 60), 236-(M^+ C_2H_2, 13), 234 (M^+-HCN, 11), 219 ($M^+-NH_2-C_2H_2$, 5), 208($M^+-C_2H_2-HCN$, 20), 171 (5), 144 (5), 143 (8), 118 (9) and 90 (12).

Condensation products of III with aromatic aldehydes in the presence of glacial acetic acid can be either Schiff bases, 2-benzalamino-3-(2-benzimidazolyl)-1,8-naphthyridines (V) or the isomeric 7-aryl-6,7-dihydrobenzimidazo [1',2' : 1,6] pyrimido [4,5-*b*] [1,8] naphthyridines (IV). The selective formation of IV is in this context explained on the basis of the ir spectra. In the ir spectra, the absence of the characteristic broad band of hydrogen on benzimidazole (3140 cm^{-1}) indicates the condensation products to be the cyclic dihydro system IV. Physical data of these compounds are given in Table 1.

The dihydronaphthyridines (IV) were smoothly oxidised by $KMnO_4$ in glacial acetic acid to 7-arylbenzimidazo[1',2':1,6]pyrimido[4,5-*b*][1,8]naphthyridines (VI), which showed the absence of NH group in the ir spectra. The mass spectrum of 7-*p*-chlorophenyl VI showed prominent peaks at m/z 381 (M^+, 25%), 299 (8), 287 (60), 277 (10), 261 (100), 246 (30), 245 (80), 244 (40), 235 (10), 218 (5) and 217 (10). Physical data of these compounds are recorded in Table 2.

Experimental

Melting points reported are uncorrected. The purity of all the compounds was checked by tlc. Ir spectra (nujol) were run on a Perkin-Elmer 283 spectrophotometer, proton nmr spectra on a Varian EM-390, 90 MHz spectrometer using TMS as the internal references, and the mass spectra on a Varian MAT CH-7 instrument at 70 eV.

2-Amino-3-(2-benzimidazolyl)-1,8-naphthyridine (III) : A mixture of 2-aminonicotinaldehyde (I, 0.1 mol) and 2-cyanomethylbenzimidazole (II, 0.1 mol) was refluxed in ethanol (20 ml) in the presence of a catalytic amount of piperidine for 0.5 h. The reaction mixture was allowed to cool and the solid thus obtained was filtered. The product was crystallised from dimethylformamide as pale yellow crystals (95%). m.p. >300° (Found : C, 69.00 ; H, 4.25 ; N, 26.91. $C_{15}H_{11}N_5$ requires C, 68.96 ; H, 4.21 ; N, 26.82%).

TABLE 1—PHYSICAL DATA OF 7-ARYL-6,7-DIHYDROBENZIMIDAZO[1',2':1,6]PYRIMIDO[4,5-*b*][1,8]NAPHTHYRIDINES (IV)

Sl. No.	R	M.p. °C	Yield %	Mol. formula	Analysis % : Found/(Calcd.) C	H	N
1.	Phenyl	>300	80	$C_{22}H_{16}N_6$	75.71 (75.64)	4.30 (4.29)	20.23 (20.05)
2.	*p*-Methoxyphenyl	>300	72	$C_{23}H_{17}N_6O$	72.91 (72.82)	4.91 (4.48)	18.35 (18.47)
3.	*p*-Tolyl	>300	76	$C_{23}H_{17}N_6$	76.15 (76.03)	4.70 (4.68)	19.30 (19.38)
4.	*p*-Chlorophenyl	>300	80	$C_{22}H_{14}N_6Cl$	68.85 (68.83)	3.70 (3.65)	18.21 (18.25)
5.	*p*-Bromophenyl	>300	80	$C_{22}H_{14}N_6Br$	61.71 (61.68)	3.30 (3.27)	16.40 (16.35)
6.	*m*-Nitrophenyl	>300	80	$C_{22}H_{14}N_7O_2$	67.15 (67.00)	3.40 (3.55)	21.36 (21.31)
7.	*p*-Nitrophenyl	>300	85	$C_{22}H_{14}N_7O_2$	67.92 (67.00)	3.62 (3.55)	21.29 (21.31)
8.	2-Thienyl	>300	60	$C_{20}H_{14}N_6S$	67.58 (67.60)	3.70 (3.66)	19.69 (19.71)

TABLE 2—PHYSICAL DATA OF 7-ARYLBENZIMIDAZO[1',2':1,6]PYRIMIDO[4,5-*b*][1,8]NAPHTHYRIDINES (VI)

Sl. No.	R	M.p. °C	Yield %	Mol. formula	Analysis % : Found/(Calcd.) C	H	N
1.	Phenyl	>300	40	$C_{22}H_{14}N_6$	75.98 (76.08)	3.69 (3.74)	20.20 (20.17)
2.	*p*-Methoxyphenyl	>300	40	$C_{23}H_{16}N_6O$	73.19 (73.20)	3.90 (3.97)	18.60 (18.56)
3.	*p*-Tolyl	>300	35	$C_{23}H_{16}N_6$	76.50 (76.45)	4.10 (4.15)	19.40 (19.39)
4.	*p*-Chlorophenyl	>300	40	$C_{22}H_{13}N_6Cl$	69.11 (69.01)	3.18 (3.13)	18.28 (18.30)
5.	*p*-Bromophenyl	>300	40	$C_{22}H_{13}N_6Br$	62.00 (61.97)	2.74 (2.80)	16.40 (16.43)
6.	*m*-Nitrophenyl	>300	40	$C_{22}H_{13}N_7O_2$	67.40 (67.34)	3.10 (3.02)	21.50 (21.42)
7.	*p*-Nitrophenyl	>300	40	$C_{22}H_{13}N_7O_2$	67.40 (67.34)	2.99 (3.02)	21.45 (21.42)
8.	2-Thienyl	>300	35	$C_{20}H_{11}N_6S$	68.10 (67.98)	3.14 (3.11)	19.70 (19.83)

General procedure for preparation of 7-aryl-6, 7-dihydrobenzimidazo[1',2' : 1,6] pyrimido [4,5-b] *[1,8]naphthyridines* (IV) : 2-Amino-3-(2-benzimidazolyl)-1,8-naphthyridine (III, 0.1 mol) and aromatic aldehyde (0.1 mol) were refluxed in glacial acetic acid (30 ml) for 2 h. The resulting solution was allowed to cool and poured onto crushed ice. The separated solid was filtered and crystallised from dimethylformamide to give IV.

7-Arylbenzimidazo [1', 2' : 1,6] pyrimido [4,5-b] *[1,8] naphthyridines* (VI) *from* IV : To a solution of IV (0.01 mol) in glacial acetic acid (20 ml), finely powdered $KMnO_4$ (3 0 g) was added. The reaction mixture was heated on a steam bath for 0.5 h. It was then filtered while hot and clear filtrate was digested with hot water (200 ml). The rapidly separated solid was filtered and crystallised from aqueous dimethylformamide to give VI.

Acknowledgement

The authors are thankful to Prof. E. V. Sundaram, Head, Department of Chemistry and Dean, Faculty of Science, Kakatiya University for providing facilities and to Dr. K. Nagarajan of of CIBA-Geigy Research Centre, Bombay for mass spectra. Thanks are also due to Dr. Kurt L. Loening, Nomenclature Director, Chemical Abstracts Service for naming the naphthyridine derivatives.

References

1. B. SREENIVASULU and K. VIJAYENDER REDDY, *Curr. Sci.*, 1977, 46, 597.
2. K. MOGILAIAH and B. SREENIVASULU, *Indian J. Chem., Sect. B*, 1982, 21, 479.
3. K. MOGILAIAH, K. VIJAYENDER REDDY and B. SREENIVASULU, *Indian J. Chem., Sect. B*, 1983, 22, 178.
4. K. MOGILAIAH, K. R. RAJU and B. SREENIVASULU, *Indian J. Chem., Sect. B*, 1981, 20, 821.
5. K. MOGILAIAH and B. SREENIVASULU, *Indian J. Chem., Sect. B*, 1982, 21, 582.
6. K. MOGILAIAH and B. SREENIVASULU, *J. Indian Chem. Soc.*, communicated.
7. N. SUZUKI and R. DOHMORI, *Chem. Pharm. Bull.*, 1979, 27, 410 (*Chem. Abstr.*, 1979, 91, 74515).
8. N. SUZUKI, Y. TANAKA and R. DOHMORI, *Chem. Pharm. Bull.*, 1980, 28, 235 (*Chem. Abstr.*, 1980, 93, 71637)
9. N. SUZUKI, *Chem. Pharm. Bull.*, 1980, 28, 761 (*Chem. Abstr.*, 1980, 93, 168191).
10. T. TABUBO, *Yakugaku Zasshi*, 1961, 81, 1812 (*Chem. Abstr.*, 1962, 57, 11665).
11. H. J. EGGERS and I. TAMM, *J. Exptl. Med.*, 1961, 113, 657.
12. V. S. MISRA, P. SHAH and V. K. SAXENA, *J. Indian Chem. Soc.*, 1982, 59, 1074.
13. P. F. JUBY, T. W. HYDYMA, M. BROWN, J. H. ESSERY and R. A PARTYKA, *J. Med. Chem.*, 1979, 22, 263.
14. W. E. BARTH, U. S. Pat. 3883653 (*Chem. Abstr.*, 1975, 83, 97364).
15. K. J. MORGAN, *J. Chem. Soc.*, 1961, 2343.
16. E. M. HAWES and D. G. WIBBERLEY, *J. Chem. Soc.*, 1967, 1565.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 891-892

Synthesis and Antitubercular Activity of Some 2-Aryl-3-[4-chlorobenzamido]-5-substituted-4-thiazolidinones

M. P. DAVE, J. M. PATEL, N. A. LANGALIA and K. A. THAKER

University Department of Chemistry, Bhavnagar University, Bhavnagar-364 002

Manuscript received 21 February 1984, revised 20 July 1984, accepted 15 August 1984

2-Aryl-3-[4-chlorobenzamido]-5-substituted-4-thiazolidinones (II, III and IV) have been prepared by condensation of Schiff bases (I) with mercaptoalkanoic acids. These compounds show antitubercular activity against $H_{37}R_v$ strain.

THIAZOLIDINONES are well known for their varied spectrum of pharmacological activities[1-4]. Some of the substituted thiazolidinones have been found to possess anaesthetic, anticonvulsant, antitubercular and sedative properties[5,6].

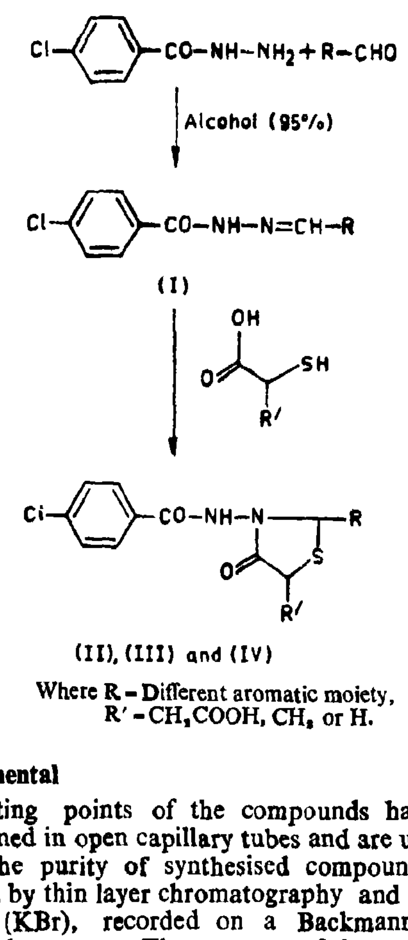
A wide variety of carboxyhydrazides has been examined for antituberculous activity. The results obtained vary drastically depending on the strain of Mycobacteria used, and emphasize the need for using a human strain, such as $H_{37}R_v$, in screening for a potential antituberculous agent for human use. Benzoylhydrazide and its nitro-, chloro- and methoxy-derivatives have been rated active against the bovine strain D_4, not significantly active against the bovine revenel strain, and active against the human strain $H_{37}R_v$[7].

Since the advent of isonicotinic acid hydrazide (INH) as a clinically effective antitubercular drug, a large number of hydrazides have been synthesised and tested for antibacterial properties[8-10]. Hydrazones obtained from hydrazides frequently act as monoamineoxidase (MAO) inhibitors. Besides, hydrazides have been associated with anthelmintic and antifungal activity[11,12].

The preparation of hydrazone from 4-chlorobenzoic acid hydrazide involved the condensation of 4-chlorobenzoic acid hydrazide with substituted aromatic aldehydes. The condensation was acomplished by heating the former with appropriate aldehyde in aqueous ethanol for a definite length of time to get the hydrazide.

The present work deals with the synthesis and pharmacological studies of some 4-thiazolidinones[13] of the type II, III and IV, the Schiff[14] bases of 4-chlorobenzoic acid hydrazide have been prepared with different aromatic aldehyde and condensed with mercapto alkanolic acid, *viz.* thioglycollic, thiomalic and thiolactic acids. When tested, these compounds (II, III and IV) showed antitubercular activity against $H_{37}R_v$ strain in Lowenstein-Jensen egg medium (4 ml).

The schematic presentation of the reaction sequences are given below.



(II), (III) and (IV)

Where R – Different aromatic moiety,
R′ – CH_2COOH, CH_3 or H.

Experimental

Melting points of the compounds have been determined in open capillary tubes and are uncorrected. The purity of synthesised compounds were checked by thin layer chromatography and infrared spectra (KBr), recorded on a Backmann IR-20 spectrophotometer. The structure of the compounds were established on the basis of their elemental analysis, counter synthesis mixed melting point and infrared spectrum. The ir spectra of compounds II, III and IV showed characteristic bands at 1640, 1600 and 1650 cm^{-1} of carbonyl stretching frequency for thiazolidinone ring system.

1-[4-Chlorobenzoyl]-2-benzylidene hydrazine (I) : To a solution of aldehyde (0.01 *M*) in ethanol (50 ml, 95%) was added 4-chlorobenzoic acid hydra-

TABLE 1—PHYSICAL AND BIOLOGICAL DATA OF COMPOUNDS II, III AND IV

Sl. No.	R	R′	Type of compd.	M.p. °C	Yield %	Antitubercular activity*, μg ml⁻¹ 0	5	30
1.	C_6H_5	H	II	190	73	+	+	−
2.	2-NO_2-C_6H_4	H	II	166	71	+	+	−
3.	4-NO_2-C_6H_4	H	II	187	68	+	+	−
4.	4-CH_3O-C_6H_4	H	II	198	70	+	+	−
5.	3,4-$(CH_3O)_2$-C_6H_3	H	II	111	75	+	+	−
6.	C_6H_5	CH_2COOH	III	240	59	+	+	−
7.	2-NO_2-C_6H_4	CH_2COOH	III	260	53	+	+	−
8.	4-NO_2-C_6H_4	CH_2COOH	III	240	55	+	+	−
9.	4-CH_3O-C_6H_4	CH_2COOH	III	177	62	+	+	−
10.	3,4-$(CH_3O)_2$-C_6H_3	CH_2COOH	III	140	51	+	+	−
11.	C_6H_5	CH_3	IV	88	65	+	+	−
12.	2-NO_2-C_6H_4	CH_3	IV	218	58	+	+	−
13.	4-NO_2-C_6H_4	CH_3	IV	96	62	+	+	−
14.	4-CH_3O-C_6H_4	CH_3	IV	191	63	+	+	−
15.	3,4-$(CH_3O)_2$-C_6H_3	CH_3	IV	800	56	+	+	−

All the compounds gave satisfactory C, H, N and S analyses.
* (+) = Inactive (no inhibition), (−) = active.

zide (0.01 *M*)[15] in ethanol (50 ml, 95%). The solution was heated for 2.5 h, cooled and worked up to get the corresponding Schiff base, I (62%), m.p. 226° (Found: N, 11.2. $C_{14}H_{11}ClN_2O$ requires N, 10.83%).

2-Phenyl-3-[4-chlorobenzamido]-4-thiazolidi-none (II): 1-[4-Chlorobenzoyl]-2-benzylidene hydrazine (0.01 *M*), dry benzene (100 ml) and thioglycolic acid (0.012 *M*) were heated under reflux for 30 h using Dean and Stark water-separator. The solvent was removed by distillation and the residue was treated with $NaHCO_3$ solution and filtered. The thiazolidinones crystallised from 95% ethanol (73%), m.p. 191° (Found: N, 8.54; S, 9.78. $C_{16}H_{13}ClN_2O_2S$ requires N, 8.42; S, 9.63%).

2-[4-Nitrophenyl]-3-[4-chlorobenzamido]-5-carboxymethyl-4-thiazolidinones (III): 1-[4-Chlorobenzoyl]-2-[4-nitro]-benzylidene hydrazine (0.01 *M*) and thiomalic acid (0.01 *M*) were condensed in presence of anhydrous zinc chloride (0.5 g) at 160° for 2 h, temperature was then raised to 180° for 30 min. The product so obtained was dissolved in sodium bicarbonate solution (4 *N*) and filtered. The filterate was reprecipitated with dilute hydrochloric acid and crystallised from 95% ethanol (55%), m.p. 240° (Found: N, 9.67; S, 7.41. $C_{18}H_{14}ClN_3O_6S$ requires N, 9.64; S, 7.35%).

2-[4-Methoxyphenyl]-3-[4-chlorobenzamido]-5-methyl-4-thiazolidinones (IV): 4-Methoxy benzaldehyde (0.02 *M*) was mixed with a solution of 1-[4-chlorobenzoyl]-2-[4-nitro]-benzylidene hydrazine (0.02 *M*) in dry benzene and refluxed for 2 h. Thiolactic acid (0.02 *M*) was then added, and refluxing continued for further 6 h. The organic layer was washed with $NaHCO_3$ solution to remove unreacted thiolactic acid, and the solvent removed under reduced pressure to get the residue which on crystallisation from 95% ethanol gave the product (56%), m.p. 191° (Found: N, 7.54; S, 8.42. $C_{18}H_{17}ClN_2O_3S$ requires N, 7.44; S, 8.63%).

Biological screening: The *in vitro* antimycobacterial activity of the synthesised compounds have been studied at 0, 5 and 30 μg ml⁻¹ (solvent: DMF) against $H_{37}R_v$ strain of *Mycobacterium tuberculosis* using Lowenstein-Jensen egg medium (4 ml). The retardation of growth rate has been studied upto 6 weeks at 37°. The procedure was duplicated using only solvent for control purpose.

The physical and biological data have been reported in Table 1.

Results and Discussion

The screening results of the *in vitro* antimycobacterial activity of the synthesised compounds show that all are inactive at 0 and 5 μg ml⁻¹ concentration, but the title compounds (II, III and IV) are active at higher concentration, *viz.* at 30 μg ml⁻¹.

Acknowledgement

Authors are thankful to Bhavnagar University for the award of research scholarships to two of them (M.P.D. and J.M.P.), and grateful to Dr. S. B. Trivedi, Director, Tuberculosis Research Centre, Amargadh for screening the samples.

References

1. W. J. DORAN and H. A. SONAL, *J. Org. Chem.*, 1938, **3**, 193.
2. L. C. CHEMOY, R. R. SMITH and S. B. BLINKHEY, *J. Am. Chem. Soc.*, 1949, **71**, 61.
3. G. L. WILLEY, *Brit. J. Pharmacol.*, 1955, **10**, 466.
4. D. R. PATEL, P. S. SATPANTHI, P. B. PATEL and J. J. TRIVEDI, *J. Inst. Chem., Calcutta*, 1976, **48**, 305.
5. H. D. TROUTMAN and L. M. LONG, *J. Am. Chem. Soc.*, 1948, **70**, 346.
6. A. R. SURREY, *J. Am. Chem. Soc.*, 1949, **71**, 3354.
7. H. H. FOX and J. T. GIBAS, *J. Org. Chem.*, 1952, **17**, 1653.
8. W. WERNER, *J. Org. Chem.*, 1953, **18**, 1933.
9. K. U. M. PRASAD, B. H. IYER and M. SIRSI, *J. Indian Chem. Soc.*, 1966, **43**, 784.
10. S. S. PARMAR and R. KUMAR *J. Med. Chem.*, 1968, **11**, 635.
11. R. CAVIER and R. RIPS, *J. Med. Chem.*, 1965, **8**, 706.
12. E. DEGNER, H. SCHEINPFLUG and H. G. SCHMELZER, Brit. Pat. 1085474/1967 (*Chem. Abstr.*, 1968, **68**, 95567).
13. A. R. SURREY, *J. Am. Chem. Soc.*, 1947, **69**, 2911.
14. A. A. CHILINGARYAN, *Tr. Leningr. Khim. Farmatsevl Inst.*, 1960, **11**, 28 (*Chem. Abstr.*, 1963, **58**, 6723).
15. M. CLAESEN, P. VANDIGCK and H. VANDER HAEGHE, *J. Pharm. Pharmacol.*, 1954, **6**, 127.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 893-894

Biological Active Agents. Synthesis of Bakuchiol Analogues

BALDEV VIG and RAM KANWAR

Department of Chemistry, Maharshi Dayanand University, Rohtak-124 001

and

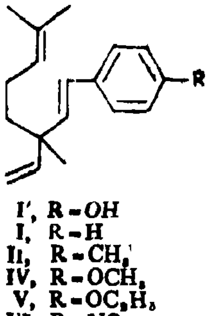
DESH RAJ ARORA

Department of Microbiology, Medical College, Rohtak

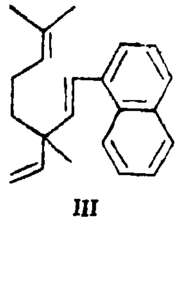
Manuscript received 2 May 1984, accepted 15 August 1984

Several bakuchiol analogues have been synthesised by preparing allyl vinyl ether of geraniol which on thermal rearrangement gave γ-δ-unsaturated aldehyde, which on further Grignard reaction with various substituted bromo aromatic compounds and dehydration gave various substituted analogues of title compounds. Their biological activities have been studied.

BAKUCHIOL has been isolated as an active oil from the seeds of *Psoralea corlifolia* Linn[1]. (Sanskrit : *Bakuchi Sungandha Kantak*, Hindi : *Babchi*). During pharmacological screening[2,3] it was noted that the oil inhibited the growth of *Staphylococcus aureus* in a concentration of 2-4 μg ml^{-1}. On the basis of chemical reactions, spectral data and synthesis[4-7], bakuchiol has been shown to be monoterpene-phenol of having the structure, 1-(*p*-anisyl)-3,7-dimethyl-3-vinyl-1,6-octadiene (I′,R=OH), b.p. 180-190°/11-15 mm. Because of its antibacterial activity it was thought of interest to prepare bakuchiol analogues and test their biological activity.



I′, R = OH
I, R = H
II, R = CH_3
IV, R = OCH_3
V, R = OC_2H_5
VI, R = NO_2



III

Geraniol was converted to its vinyl ether through equilibration with ethyl vinyl ether in presence of mercuric acetate. Pyrolysis of the allyl-vinyl system in a sealed tube under nitrogen atmosphere generated 3,7-dimethyl-3-vinyl-oct-6-enal. The resulting γ-δ-unsaturated aldehyde was subjected to Grignard reaction with different *para*-substituted phenyl magnesium bromide to produce the corresponding carbinol which was subsequently dehydrated under milder conditions using $POCl_3$ in pyridine at low temperature. The final products were chromotographed over alumina before distillation under reduced pressure. The purity of the compounds were checked on tlc and the structure of final analogues and various intermediates were checked through ir and ^{1}H nmr spectroscopy. Various analogues of bakuchiol prepared are shown in Table 1.

TABLE 1

Sl. no.	Compd.	R	Mol. formula	B.p. °C/8 mm
1.	I	H	$C_{18}H_{24}$	170-175°
2.	II	CH_3	$C_{19}H_{26}$	175-180°
3.	IV	OCH_3	$C_{19}H_{26}O$	175-180°
4.	V	OC_2H_5	$C_{20}H_{28}O$	185-190°
5.	VI	NO_2	$C_{18}H_{23}NO_2$	180-185°
6.	III		$C_{22}H_{26}$	190-195°

The compounds gave satisfactory elemental analysis.

Antibacterial activity :

Antibacterial activity against *Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Salmonella typhi*, and *Pseudomonas aeruginosa*, and antifungal activity against *Candida albicans, Cryptococcus neoformans, Trichophyton mentagrophytes, Microsporum canis* and *Aspergillus flavus* of all the compounds (I-VI) were studied as follows.

10 mg of each compound was dissolved in 10 ml each of absolute alcohol. Filter paper discs (6 mm dia.) cut from Whatman No. 1 were dipped in each of the above solution and the solvent was allowed to evaporate. Nutrient agar plates were inoculated with various bacteria, *C. albicans* and *C. neoformans*. On each plate one disc from each compound was applied and the plates inoculated with bacterial cultures were incubated at 37° for 18 h and those inoculated with fungi (*C. albicans* and *C. neoformans*) at 37° for 96 h. Zones of inhibition around the discs were noted. Those showing these zones were taken as sensitive. Minimum inhibitory

TABLE 2—MINIMUM INHIBITORY CONCENTRATION OF COMPOUNDS (I-VI) IN $\mu g\ ml^{-1}$ AGAINST VARIOUS BACTERIA AND FUNGI

Sl. no.	Organism	Minimum inhibitory concentration in $\mu g\ ml^{-1}$ Compound number					
		I	II	III	IV	V	VI
1.	*S. aureus*	–	–	neat	–	–	–
2.	*B. subtilis*	100	100	125	–	300	50
3.	*E. coli*	–	–	neat	–	100	–
4.	*S. typhi*	–	–	neat	–	–	–
5.	*P. aeruginosa*	–	–	neat	–	–	–
6.	*C. albicans*	neat	neat	–	neat	–	–
7.	*C. neoformans*	neat	neat	125	neat	–	200
8.	*T. mentagrophytes*	>1000	100	125	>1000	>1000	>1000
9.	*M. canis*	150	125	>1000	50	50	100
10.	*A. flavns*	>1000	>1000	>1000	25	25	>1000

concentration (M.I.C.) of the compounds against the bacteria and fungi which were found to be sensitive to them in neat concentration were studied by serial plate dilution method. Minimum concentration of the compound showing no growth was taken as M.I.C. The M.I.C. of these compounds against *T. mentagrophytes*, *M. canis* and *A. flavus* were studied directly by serial dilutions of these compounds in Sabourand's dextrose agar and studied as above. Results of the present study indicate that the compounds are active against various bacteria and fungi. Compound III was the most active and showed antibacterial (gram-positive and gram-negative) and antifungal activity.

Juvenile hormone activity: All the compounds were tested for their JH activity on common Indian red cotton bug. The treatment was given within 24 h of moulting to the fifth instars. Perfect adults were scored as zero. An abnormal adult that retained any of the fifth instar character scored one, one that died during moulting scored two and which could not moult scored three. The score of four was obtained by sixth instar. Average rating was calculated by multiplying the number of fifth instars by their numerical activity rating and divided the sum by the number of insects tested. The dead insects were excluded. The activities of the various compounds are given in the Table 3.

TABLE 3—JUVENILE HORMONE ACTIVITY OF ANALOGUES OF BAKUCHIOL (I-VI) NUMBER OF INSECT = 10, DOSE % IN ACETONE (μl) = 6

Bakuchiol analogue	Dead	Activity response					Activity index
		0	1	2	3	4	
I	0	2	1	1	2	4	2.5
II	0	1	1	1	4	3	2.7
III	1	2	0	1	2	4	2.6
IV	0	1	1	1	1	6	3.0
V	0	1	0	2	2	5	3.0
VI	0	1	0	2	1	6	3.1

Acknowledgement

The authors wish to thank Dr. R. K. Nigam, Head of the Department of Chemistry for providing facilities. The authors would also like to extend thanks to Microbiology Department, Medical College, Rohtak for antibacterial activity of the compounds.

References

1. G. MEHTA, U. R. NAYAK and SUKH DEV, *Tetrahedron Lett.*, 1966, 4561 ; *Tetrahedron*, 1973, **29**, 1119.
2. C. GUPTA, C. L. BHATIA, C. L. CHOPRA, A. NATH and C. CHOPRA, *R. R. L. Bull. Jammu*, 1962, **1**, 59.
3. N. GAIND, R. N. DAR and R. N. KAUL, *Indian J. Pharm.*, 1964, **26**, 141.
4. A. S. C. PARKASH RAO, V. K. BHALLA, U. R. NAYAK, and SUKH DEV, *Tetrahedron*, 1973, **29**, 1127.
5. N. P. DAMODARAN and SUKH DEV, *Tetrahedron Lett.*, 1967, 2897.
6. J. CARNDUFF and J. A. MILLER, *Chem. Commun.*, 1967, 606.
7. O. P. VIG, A. K. VIG, O. P. CHUGH and K. C. GUPTA, *J. Indian Chem. Soc.*, 1976, **53**, 368.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 895-896

Chemical Composition of the Essential Oil of *Carum anethifolium* Benth.

P. JOSHI, A. K. PANT and C. S. MATHELA*

Chemistry Department, Kumaun University, Nainital-263 002
and
VASU DEV

Department of Chemistry, California State Polytechnic University, Pomona, California-91768, U.S.A.

Manuscript received 29 March 1984, accepted 15 August 1984

A gas chromatography/mass spectroscopy study of the essential oil of *Carum anethifolium* Benth. shows the presence of 11 monoterpene hydrocarbons (80%), 9 monoterpenoids, 6 sesquiterpene hydrocarbons, and 2 sesquiterpene alcohols. Of these, 22 compounds have been identified. The monoterpens, *viz.* β-phellandrene, γ-terpinene and *p*-cymene are the major constituents.

THE genus *Carum* includes about 30 species and is distributed in temperate and sub-tropical regions. Four species of this genus in India have been reported, out of which two grow in Nainital[1,2], *Carum anethifolium* Benth. is an annual herb and is widely distributed around Nainital, mostly in open and slopy areas[3]. The physico-chemical properties of the essential oil from *Carum anethifolium* have been reported[3] but there has been no report on the chemical composition. However, the work so far reported on the chemical composition of the essential oil from *Carum carvi* shows carvone, thymol, carvacrol and γ-terpinene as the main constituents (in seeds). Our investigation confirmed the absence of carvone and carvacrol, and the presence of γ-terpinene (22.42%) and thymol (1.83%) in the essential oil from *C. anethifolium*. This communication reports the identification of 22 compounds in the oil from *Carum anethifolium* (aerial part).

Experimental

Plant material : *Carum anethifolium* was collected from Nainital in June (before flowering) and August (with flowers). The essential oil extracted in the month of June was taken for determining the chemical composition.

Extraction of oil : The essential oil was obtained by steam distillation of the fresh plant material extracted from water with pentane, dried over anhydrous Na_2SO_4 and the solvent distilled off. The physico-chemical properties of the oil were determined[4].

Gc analysis : The gas chromatography of oil was performed on Varian 3700 gas chromatograph with a flame ionization detector using a 35 m glass capillary column coated with OV-101. The percentage of various constituents was calculated from the peak areas.

Gc/ms analysis : The oil was analysed by gas chromatography/mass spectrometry using J and W fused silica capillary column (coated with DB-5, column dimension 30 m×0.25 mm) and He as carrier gas (10 lb in^{-2}). The ionization energy was 70 eV. Column temperature was programmed at 2° min^{-1} from 60° for the first 25 min, 4° min^{-1} after 25 min and finally isothermally at 225°. The sample was taken in CH_2Cl_2 for injection. Atleast 28 peaks were recorded in the gas chromatogram from RT 13.10 to 45.05 min. The mass spectra corresponding to the gc peaks were recorded. The mass spectra were compared with the ms of authentic samples and those available in the literature[5-9].

Results and Discussion

Physico-chemical properties of the oil were: specific gravity 0.8068, refractive index 1.4952, acid value 1.2, ester value 2.5, ester value after acetylation 31.0, and carbonyl value 1.0. The oil yield from fresh plant material was 0.14% and 0.24% during the months of June and August, respectively.

The results of gc/ms analysis of the oil are given in Table 1. Eleven monoterpene hydrocarbons constituted 80% of the oil, β-phellandrene, γ-terpinene and *p*-cymene being the major constituents. Nine oxygenated monoterpenoids accounted for 8.53% of the oil. Six sesquiterpene hydrocarbons form 4.96% of the oil, α-humulene and *trans*-α-bergamotene being dominant among these. Two sesquiterpene alcohols constitute 1% of the oil. Thymol, a phenol amounted only 1.83% while the other phenolic constituents, reported in other *Carum* oils were not detected in this oil.

TABLE 1—COMPOSITION OF ESSENTIAL OIL OF *C. anethifolium*

Compound	Gc peak	RT min	% in the oil
Monoterpene hydrocarbons			
β-Ocimene-X	1	13.10	2.48
C_9H_{12}	2	13.80	0.13
Myrcene	3	14.20	1.16
α-Fenchene	4	15.23	1.12
p-Cymene	5	16.15	16.08
Limonene	6	16.67	7.08
α-Phellandrene	7	17.98	0.58
γ-Terpinene	8	18.63	22.42
β-Phellandrene	9	20.37	28.34
$C_{10}H_{14}$	10	22.35	0.53
$C_{10}H_{14}$	11	24.20	0.08
Oxygenated monoterpenoids			
Myrtenol	12	24.50	3.07
Dihydrocarvone	13	24.87	0.12
Dihydrocuminyl alcohol	14	25.88	0.24
$C_{10}H_{18}O$ (alcohol)	15	26.40	0.27
Carveol	16	26.93	0.21
Thymol	17	27.20	1.83
$C_{10}H_{18}O$ (alcohol)	18	28.08	0.48
Borneol	19	32.10	1.19
Unidentified (MW 166)	20	37.30	1.12
Sesquiterpene hydrocarbons			
α-Humulene	21	38.67	1.26
Cedrene	22	40.08	0.77
trans-α-Bergamotene	23	40.58	1.51
Aromadendrene	24	41.02	0.60
Cuparene	25	41.08	0.41
β-Bisabolene	26	42.35	0.41
Sesquiterpene alcohols			
trans-Bergamota-2,12-dien-14-ol	27	43.02	0.52
β-Eudesmol	28	45.03	0.48

Acknowledgement

The authors are thankful to Dr. D. Forkey, California State University, Sacramento for gc/ms and Dr. Y. P. S. Pangtey, Department of Botany, Kumaun University for identification of the plant. One of the authors (P.J.) is grateful to U.G.C., New Delhi for the award of Junior Research Fellowship.

References

1. R. K. GUPTA, "Flora Nainitalensis", Navyug Traders, New Delhi, 1968, p. 150.
2. R. STRACHEY, "Catalogue of the Plants of Kumaon", Periodical Experts, New Delhi, 1974, p. 174.
3. P. SINGH and G. K. SINHA, *Indian Perfumer*, 1976, 1, 20.
4. E. GUENTHER, "The Essential Oils", Van Nostrand, New York, 1955, Vol. 1, p. 236.
5. C. S. MATHELA, personal collection of mass spectra of terpenoids.
6. R. RYHAGE and E. VON SYDOW, *Acta Chem. Scand.*, 1963, 17, 2025.
7. E. VON SYDOW, *Acta Chem. Scand.*, 1963, 17, 2504.
8. Y. MASADA, "Analysis of Essential Oil by Gas Chromatography and Mass Spectrometry", John Wiley, New York, 1976.
9. M. G. MOSHONAS and E. D. LUND, *Flavour Industry*, 1970, 1, 375.

Notes

Coordination Compounds of Bivalent Copper with Benzhydrazide of 5-Bromosalicylaldehyde, 2-Hydroxy-5-methyl-benzophenone and 2, 4-Dihydroxy-valerophenone†

V. K. RASTOGI*

Department of Physics, Meerut College, Meerut-250 001

and

R. C. SAXENA, A. K. KOTNALA and J. N. RASTOGI

Department of Chemistry, M. M. College, Modinagar-201 204

Manuscript received 6 February 1982, revised 19 May 1983, accepted 1 September 1983

In view of the analytical utility[1,3] and biological activity[2] of the hydrazones we have isolated some Cu^{II} complexes with benzahydrazide of 5-bromo-salicylaldehyde, 2-hydroxy-5-methylbenzophenone and 2, 4-dihydroxyvalerophenone. The present note describes the preparation and characterisation of these compounds.

Experimental

Preparation of ligands: The starting materials, ethylbenzoate, 5-bromosalicylaldehyde, 2-hydroxy-5-methylbenzophenone and 2, 4-dihydroxyvalerophenone were of high purity. The compounds were synthesised by the general method reported in the literature.

Preparation of complexes: An ethanolic solution of substituted hydrazones were reacted with copper chloride solution in ethanolic acetone in stoichiometric ratio, and the mixture was refluxed for 2 h over a water-bath after raising the *p*H of the mixture with NaOH solution (1%). On keeping for some time coloured compounds separated out which were filtered, washed with water and dried *in vacua.* The results of the elemental analyses for the complexes are presented in Table 1.

Results and Discussion

The analytical results (Table 1) indicate that the complexes have the general formula $[Cu(L)]_2$. The magnetic data show that the complexes are paramagnetic with an effective magnetic moment in the range of 1.88-1.83 B.M., revealing square planar (D_{4h}) geometry around the metal ion.

The electronic spectra of the complexes show a broad peak in the region 16580-18867 cm^{-1}. The peaks observed in the regions 27000-28571 and ~35714 cm^{-1} in the complexes may be charge transfer bands. The bands at ~25000 and 14900 cm^{-1} may be assigned to the transition $2E \rightarrow 2T_2$ of the Cu^{II} and intra-ligand charge transfer, respectively[4].

The ir spectral data of ligands and the complexes have been interpreted on the lines of previously reported data. The ligands are capable of undergoing keto$\rightleftharpoons$enol tautomerism, and hence, they can coordinate in either of these two forms. The spectral studies show that the ligand molecules coordinate to the metal in the enolic form.

The ligands display frequencies in the regions 3400-3300 (enolic OH) and 1350-1300 cm^{-1} (phenolic C—O). The absence of ν_{OH} and negative shift of ν_{O-O} bands in the complexes suggest the deprotonation of the enolic hydrogen. A strong band at ~1600-1630 cm^{-1} in the free ligands is attributable to C=N linkage. In complexes this band is shifted towards lower frequenoy region suggesting that the imine nitrogen atom is coordinated to the metal ion[5]. Bonding of the nitrogen atom to Cu^{II} ion have been further substantiated by the appearence of ν_{M-N} at 500-450 cm^{-1} region. Bands at ~3500 (phenolic OH), 1510-1550 (C—O) and 1380 cm^{-1} (C—O and C—C stretch) were observed in the spectra of the free ligands. On complexation the frequency of OH disappears[6], while that of C—O decreases considerably, indicating the removal of proton during chelation. This has been further supported by the observation of ν_{M-O} band in the far-infrared region, in agreement with the earlier observations[7]. Thus, from the above study, it may be concluded that the

TABLE 1—ANALYTICAL, MAGNETIC AND ELECTRONIC SPECTRAL DATA OF COMPLEXES

Compound	Analysis % : Found/(Calcd.)				μ_{eff}	$2B_{1g} \rightarrow$	
	Metal	C	H	N	B.M.	$2A_{1g}$	$2E_g$
$[Cu(C_{14}H_9N_2O_2Br)]_2$	17.28 (16.70)	45.59 (44.15)	2.29 (2.36)	7.61 (7.36)	1.83	18867	28571
$[Cu(C_{21}H_{16}N_2O_2)]_2$	16 86 (16.23)	61.98 (64 36)	4.22 (4.08)	7.41 (7.15)	1.85	17470	27690
$[Cu(C_{18}H_{18}N_2O_3)]_2$	17.55 (17.01)	59.80 (57.82)	4.68 (4.82)	7.24 (7.49)	1.88	16580	27000

* On leave from Molecular Spectroscopy Research Laboratory, Lajpat Rai College, Sahibabad-201 005.

† Paper presented at the Annual Convention of Chemists, Madras, 1981.

ligands act as tridentate and the coordinating sites are phenolic OH, imine nitrogen and enolic OH.

Acknowledgement

The authors are thankful to Dr. A. N. Pandey, Department of Physics, Meerut College and to (Miss) Anita for helpful discussion. One of the authors (V.K.R.) is thankful to U.G.C., New Delhi for the award of Teacher Fellowship.

References

1. F. A. French and E. D. Blanz, *Chem. Abstr.*, 1968, **68**, 297096.
2. S. Bhader, S. P. Singh and R. S. Verma, *Indian J. Pharm. Sci.*, 1979, **41**, 36.
3. H. L. Ray, B. S. Garg and R. P. Singh, *J. Chin. Chem. Soc.*, (*Taipei*), 1976, **23**, 47.
4. S. V. Cheat and T. N. Waters, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1221.
5. N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3781.
6. S. J. Gruber, C. N. Harrisand and E. Sinu, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3379.
7. J. Reedizk, *Inorg. Chim. Acta*, 1971, **5**, 687.

Characterisation of Some Copper(I) and Silver(I) Complexes Containing Tetraisothiocyanato-*N*-diaminechromate(III)

(Mrs.) P. R. SHUKLA, B. B. AWASTHI

and

RACHANA RASTOGI

Chemistry Department, Lucknow University, Lucknow-226 007

Manuscript received 7 October 1983, revised 22 May 1984, accepted 20 September 1984

DURING our studies on those coordination compounds in which both cation and anion are complex ions, a series of complexes of various metal(II) ions with amines, oximes, and schiff bases containing the anions, such as nitrosopentacyanoferrate(II) and hexacyanoferrate(II) ions were prepared and characterised[1-4]. The present note records the synthesis and characterisation of eight copper(I) and silver(I) complexes containing the tetraisothiocyanato-*N*-diaminechromate(III) ion. These complexes have been assigned to have planar structures on the basis of their magnetic, infrared and electronic spectral data.

Experimental

The complexes were prepared by suspending copper(II) sulphate or silver(I) nitrate in distilled water and adding required amount of ligand in methanol or water. The solution was then refluxed for 4 h and then treated with ammonium tetraisothiocyanato-*N*-diaminechromate(III) and refluxed again for 2 h. In case of copper(II), sulphurous acid was added to reduce it to copper(I) before refluxing with the ligand. Finally, the complex under study was crystallised out from the solution using petroleum ether and diethyl ether mixture.

Results and Discussion

The molecular formulae proposed for the various complexes are given in Table 1 and are supported by the analytical and molar conductance data. The coordination of various ligands to the two metal ions has been inferred by the infrared data as follows.

(i) In all the complexes a sharp band appears around 3300 cm^{-1} which is due to the presence of ammonia, ethylenediamine, urea and thiourea in the complexes. It is assigned to be the N—H stretch, the negative shift of which is due to the coordination of the above ligands to the metal ions.

(ii) In addition to this, all the complexes also contain two very sharp bands at 2080 and 810 cm^{-1} which are characteristic of a N-coordinated thiocyanate ion[5,6].

TABLE 1—ANALYTICAL AND MOLAR CONDUCTANCE DATA

Sl. no.	Complex	Colour	Analysis % : Found/(Calcd) M	thiocyanate	Cr	N	Molar conductance in $PhNO_2$ Ω^{-1}
1.	$[Cu(Py)_2[Cr(NCS)_4(NH_3)_2]$	Reddish yellow	11.23 (11.76)	44.5 (43.01)	10.00 (9.63)	28.42 (28.75)	19.89
2.	$[Cu(en)[Cr(NCS)_4(NH_3)_2]$	Yellow	13.92 (14.37)	50.52 (52.56)	10.5 (11.77)	24.93 (25.35)	20.50
3.	$[Cu(urea)_2][Cr(NCS)_4(NH_3)_2]$	Yellow	13.02 (12.64)	46.92 (46.27)	11.00 (10.36)	27.54 (27.90)	24.65
4.	$[Cu(thiou)_2][Cr(NCS)_4(NH_3)_2]$	Orange	12.51 (12.12)	45.00 (44.32)	10.2 (9.92)	26.21 (26.72)	19.50
5.	$[Ag(Py)_2][Cr(NCS)_4(NH_3)_2]$	Pink	18.92 (18.47)	40.2 (39.74)	9.30 (8.90)	19.85 (19.17)	21.05
6.	$[Ag(en)][Cr(NCS)_4(NH_3)_2]$	Violet	23.00 (22.2)	48.20 (47.80)	11.10 (10.69)	22.94 (23.04)	Insoluble
7.	$[Ag(urea)][Cr(NCS)_4(NH_3)_2]$	Brownish pink	20.10 (19.76)	43.60 (43.52)	10.10 (9.52)	25.12 (25.64)	Insoluble
8.	$[Ag(thiou)_2][Cr(NCS)_4(NH_3)_2]$	Pink	18.97 (19.0)	41.30 (40.16)	9.40 (8.99)	24.95 (24.21)	Insoluble

(iii) The complexes 3 and 7 contain urea which is capable of coordinating through nitrogen or oxygen. In both the complexes a broad band appears at 3320 cm^{-1} (N—H stretching) and its broadening is due to its coupling with the corresponding band of ammonia. The carbonyl stretching frequency is observed at 1660 cm^{-1} and its negative shift corresponds to the coordination of urea through oxygen. The complexes 4 and 8 contain thiourea as ligand and in their spectra two distinct bands appear at 1500 and 730 cm^{-1} assigned to C—N and C—S stretches. The increase in the former and decrease in the later support the coordination of thiourea through sulphur[7,8].

As copper(I) and silver(I) ions belong to d^{10} or spin-paired configurations, the magnetic moment values of the complexes are expected to correspond only to chromium(III) ion with three unpaired electrons and thus fall around 3.89 B.M. The electronic spectra also shows bands at 25.00, 19.00 and 13.50 kK characteristic of octahedrally coordinated chromium (III), as no d-d bands are possible theoretically for the above metal(I) ions.

Acknowledgement

The authors are thankful to Prof. V. S. Misra, Head, Chemistry Department, Lucknow University for providing facilities. One of the authors (B.B.A.) is thankful to C.S.I.R., New Delhi for the award of Junior Research Fellowship.

References

1. P. R. Shukla, S. Misra and G. Narain, *J. Indian Chem. Soc.*, communicated.
2. P. R. Shukla, G. Narain and A. K. Shakya, *J. Indian Chem. Soc.*, communicated.
3. G. Narain, T. M. Agnihotri and P. R. Shukla, *J. Indian Chem. Soc.*, communicated.
4. G. Narain and A. M. Shakya, *J. Indian Chem. Soc.*, communicated.
5. S. Guru, B. K. Mahapatra and B. Paul, *J. Indian Chem. Soc.*, 1977, **54**, 337.
6. J. Naka and S. Mizushima, *Bull. Chem. Soc. Jpn.*, 1955, **28**, 589.
7. A. Yamaguchi, *J. Am. Chem. Soc.*, 1958, **80**, 527.
8. N. R. Kunchun and M. R. Truter, *J. Chem. Soc.*, 1958, 3478.

Organophosphonic Acids as Complexones. Part-VI. Reactions of Hydroxyethylidenediphosphonic Acid with Bivalent Metal Ions

D. M. PURI*, B. VENKATESWARA RAO, NEELAM PALTA and S. N. DUBEY

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

Manuscript received 26 April 1983, revised 2 May 1984, accepted 20 September 1984

In continuation to our work on metal derivatives of organophosphonic acids[1], we report here the synthesis and structural studies of metal derivatives of hydroxyethylidenediphosphonic acid in 1 : 1 molar ratio. In the present investigation, reactions with bivalent metals, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} have been carried out.

Experimental

Phosphorus trichloride and glacial acetic acid (B.D.H.) and bivalent metal acetates (B.D.H., AnalaR) were used as such.

Preparation of ligand: The ligand, HEDP, was prepared as reported earlier[1] and was also obtained as an aqueous solution from M/s Aquapharm (India) as a gift.

Preparation of metal derivatives: Aqueous solution of the acid (1 mol) was added to metal salt solution (1 mol) with constant stirring at room temperature. The precipitation was effected by dropwise addition of acetone. The precipitates were filtered and washed with distilled water containing acetone and then dried at 70-80° till constant weight. The compounds were neither soluble in water nor in any other common organic solvents. These compounds also did not melt when heated even upto 270°. Elemental analyses data, using conventional methods, and colour of the compounds have been given in Table 1.

TABLE 1—PHYSICAL STATE, ELEMENTAL ANALYSES AND MAGNETIC SUSCEPTIBILITY DATA

Compound	Colour and State	Analysis % : Found/(Calcd.) M	P	μ_{eff} B.M.
$MnHEDP.H_2O$	White solid	19.93 (19.83)	22.28 (22.38)	5.67
$Co HEDP.2H_2O$	Pink solid	19.38 (19.71)	21.06 (20.73)	5.6
$Ni HEDP.2H_2O$	Green solid	19.94 (19.65)	19.91 (20.75)	3.3
$Cu HEDP.2H_2O$	Blue solid	21.29 (20.94)	20.34 (20.42)	2.02
$Zn HEDP.2H_2O$	White solid	20.97 (21.40)	20.10 (20.30)	—
$Cd HEDP.2H_2O$	White solid	31.94 (31.89)	17.39 (17.59)	—

Ir spectra (nujol, KBr) were taken on a Beckman IR-20 spectrophotometer. Diffuse reflectance spectra were run on an Unicam SP-700 spectrophotometer with a standard reflectance accessory, using MgO as the reference. Magnetic measurements were made on Gouy balance.

Thermal analysis of the compounds were done in the atmosphere of air at National Chemical Laboratory, Pune. The specimens were heated at the rate of 10° min^{-1} in 20-1000° range, and heated alumina was used as the standard.

Results and Discussion

Different bands of the free ligand and its complexes in their infrared spectra have been given in Table 2. Phosphoryl frequency (1170-1200 cm^{-1}) of the free ligand is lowered on coordination of the phosphoryl oxygen to the metal atoms of either the same or other molecules[2]. δ_{OOH} mode (1035 cm^{-1}) of the free ligand HEDP is displaced to higher

frequency and is presumably due to coordination of hydroxyl oxygen to the metal atoms without any loss of hydrogen[3]. A single 930 cm^{-1} band in free HEDP due to $\nu_s(PO_3)$ splits into two components at 930 and 950 cm^{-1} on complex formation, suggesting the presence of two types of PO_3 groups. The 995 cm^{-1} band in the complexes is due to coordinated phosphonic group. Antisymmetric vibrational bands $\nu_{as}(PO_3)$ are observed in the 1100-1150 cm^{-1} region. A band at 440-400 cm^{-1} region in the far-infrared spectra of copper(II)-, nickel(II)- and cobalt(II)-HEDP complexes (Table 2) was assigned to ν_{M-O} vibrations[4].

TABLE 2—INFRARED SPECTRAL DATA FOR FREE LIGAND AND ITS DIFFERENT BIVALENT METAL DERIVATIVES

Assignments	HEDP	Mn^{II}	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Cd^{II}
δ_{COH}	1035	1050	1050	1050	1055	1050	1050
ν_{P-O}	1170 br 1204 br	1150	1150	1155	1150	1150	1150
$\nu_{sym}PO_3$	930	990 920	985 945	950 br	995 930	950 920	950 930
$\nu_{asym}PO_3$	1020	1090	1120	1100	1150	1090	1100
ν_{-OH_2}	3500	3440	3430	3400	3400	3370	3440
δ_{OH_2}	—	1625	1630	1650	1630	1630	1630
ν_{M-O}	—	—	440	440	400	—	—

br = Broad.

Thermal analysis : Since the general scheme of thermal decomposition is the same for all complexonates, only the derivatogram of cobalt(II) salt has, therefore, been given in Fig. 1.

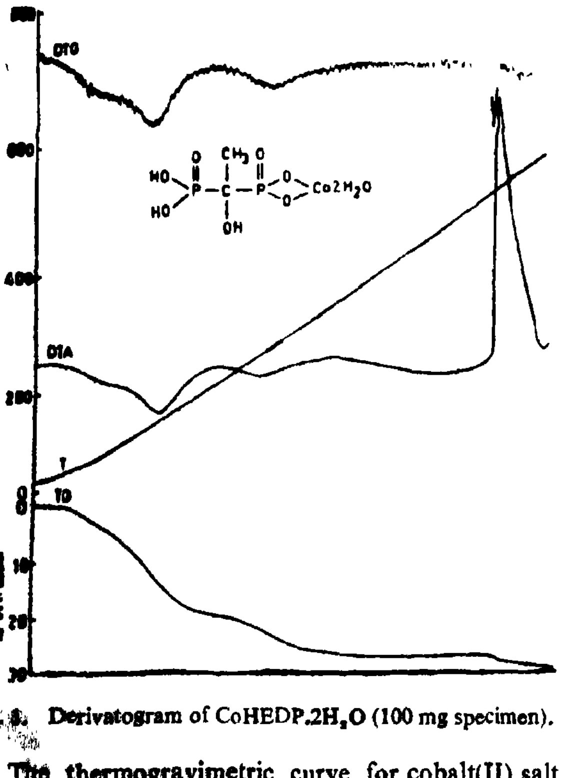


Fig. 1. Derivatogram of CoHEDP.2H$_2$O (100 mg specimen).

The thermogravimetric curve for cobalt(II) salt shows that it is stable at room temperature. There is continuous mass loss of 18% (theoretically 18.06%) upto 180° and this corresponds to loss of three molecules of water. It is accompanied by endothermic effect with the minima at 150°. Out of these three water molecules, two are water of crystallisation and the third is lost perhaps from the ligand itself. The second mass loss of 9% takes place between 240 and 335° and is endothermic in nature having the minima at 280° and an inflection at 335°. Thus total mass loss is 27% (theoretical 27.7%) which indicates that the final product of thermal decomposition is $CoO.P_2O_5$.

Magnetic moment and electronic spectra : Magnetic moment of cobalt, nickel, copper and manganese complexes have been found to be 5.6, 3.3, 2.02 and 5.67 B.M., and are within the ranges required for spin-free d^7, d^8, d^9 and d^5 systems, respectively. In case of cobalt complex magnetic moment is almost temperature independent. These values suggest the complexes to be octahedral and that the metal ions are well separated having no spin-spin interaction.

Electronic spectral data permit an unambigous structural assignments. The diffuse reflectance spectrum of cobalt(II) complex shows a broad band at 8500 cm^{-1} and another at 19420 cm^{-1} due to $^4T_{2g}(F) \leftarrow {}^4T_{1g}$ and $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ transitions, respectively and are in agreement with octahedral configuration. Similar suggestions were also made by Dunn as well as Lever[5]. A shoulder at 21050 cm^{-1} on the principal band may be due either to lower symmetry component of ligand field or to the presence of. spin-forbidden transitions[6]. In the case of nickel(II) complex spectrum, three bands at 8230, 13517 and 25970 cm^{-1} were observed arising from the transition for $^3A_{2g}$ ground state to excited levels $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$, respectively. Electronic spectrum of copper(II) complex showed one transition at 13330 cm^{-1} due to distortion in octahedral symmetry[6]. Another band at 16310 cm^{-1} was also observed.

ZnL.2H$_2$O and CdL.2H$_2$O : As expected for d^{10} system these are diamagnetic in nature.

In view of the studies made so far and also from the properties of the compounds, like their insolubility in different common organic solvents and their very high melting points (> 270°), a general polymeric octahedral structure for the compounds is indicated.

Acknowledgement

We are thankful to Prof. V. Yatirajam, Chairman of the Department of Chemistry for providing facilities. One of the authors (B.V.R.) is thankful to Indian National Science Academy, New Delhi for the award of Junior Research Fellowship.

References

1. N. PALTA and D. M. PURI, *Indian J. Chem., Sect. A*, 1982, 21, 624.
2. V. P. KHRAMOV and A. A. KOL'TSOV, *Russ. J. Inorg. Chem.*, (*Engl. Transl.*), 18, 1567; T. F. CHERNICHENKO and N. I. MIKHAILICHANKO, *Chem. Abstr.*, 1979, 90, 47662.
3. L. J. BELLAMY, "The Infrared Spectra of Complex Molecules', Nethuen and Co., London, 1958; A. V. KOTOV and L. A. GRIBOV, *Chem. Abstr.*, 1969, 70, 52662; N. M. DYATLOVA, U. V. MEDYNTSEV, T. YA. MEDVED and M. I. KABACHNIK, *Chem. Abstr.*, 1968, 69, 39184.
4. N. SAHA and P. BHATTACHARYA, *Indian J. Chem., Sect. A*, 1982, 21, 574.
5. T. M. DUNN in "Modern Coordination Chemistry, Principles and Methods', eds. J. LEWIS and R.G. WILKINS, Interscience, New York, pp. 290, 406, 450; A. B. P. LEVER, "Inorganic Electronic Spectroscopy", Elsevier, 1968, pp. 318, 321, 333-334.
6. S. V. TAIWAWADI, A. P. SINGH and K. K. NARANG, *Indian J. Chem., Sect. A*, 1982, 21, 644; W. B. LEWIS, M. ALEI and C. V. MORGAN, *J. Chem. Phys.*, 1960, 45, 4003; R. C. VAN LANDSCHOVR, J. A. M. VAN HEAT and J. RSEDISIC, *J. Inorg. Nucl. Chem.*, 1976, 38, 851.

Role of π-interaction in Ternary Complexes of Zinc(II) or Cadmium(II)+2,2'-Bipyridyl+Amino Acids

J. D. JOSHI

Department of Chemistry, South Gujarat University, Surat-395 007

Manuscript received 23 December 1983, revised 29 June 1984, accepted 20 September 1984

MIXED ligand complexes MAL, where M=Ni^{II}, Cu^{II}; A=2,2'-bipyridyl or 1,10-phenanthroline; and L = amino acids, have been studied earlier[1]. In the present investigation an attempt has been made to determine the stability constants of the title systems using modified form of Irving-Rossotti titration technique. The $[M(2,2'\text{-bipy})]^{2+}$, 1 : 1 complex formed before pH~4 and stable up to pH~8 where the secondary ligand gets coordinated. Formation of 1 : 1 complexes of both $[Ni(2,2'\text{-bipy})]^{2+}$ and $[Zn(2,2'\text{-bipy})]^{2+}$ at low pH and their stability at high pH has been shown earlier[3,4].

Experimental

All the reagents used were of A.R. quality. Metal perchlorates were used in the present study to avoid the complexing tendency of the anion.

The experimental set-up and calculations described by Bhattacharya *et al.*[5] were employed. The ionic strength was maintained at 0.2 *M* in each case. Systronics 355 digital pH meter was employed for pH measurements. Potentiometric titrations were carried out at 30° using 0.2*M* NaOH.

The interpretation of the potentiometric curves was similar to that reported[1]. From the titration data $\bar{n}_H$, $\bar{n}$ and P_L were calculated as described earlier[5]. Precise values of K^{MA}_{MAL} were determined by the method of averages* and the values are presented in the Table 1.

Results and Discussion

The order of the formation constants of the mixed ligand chelates is the same as that for the binary complexes. It is observed that the values of K^{MA}_{MAL} are nearly equal to K^{M}_{ML}. This can be explained in terms of secondary ligands basicities. The order of mixed ligand formation constant is, glycine ≈ α-alanine ≈ leucine; valine ≈ serine≈threonine ≈ methionine.

The higher values of mixed ligand formation constants can be explained by the special behaviour of 2,2'-bipyridyl. The 2,2'-bipyridyl molecule is bound to the metal ion by σ-bonding. Besides that there is also π-bonding formation by the back donation of electrons from M→L. The dπ-pπ interaction has been observed by earlier workers[7]. The positive charge on the metal ion in $[M(2,2'\text{-bipy})]^{2+}$ and $[M(aq)]^{2+}$ complexes is same, because the dπ-pπ interaction does not allow the concentration of electrons on the metal ion to increase significantly. Therefore, the electronegativity of the metal ion in $[M(2,2'\text{-bipy})]^{2+}$ remains same as in $[M(aq)_n]^{2+}$. So, the tendency of the secondary ligand L to combine with $[M(2,2'\text{-bipy})]^{2+}$ and $[M(aq)_n]^{2+}$ is comparable. Therefore, K^{MA}_{MAL} values are nearly equal to K^{M}_{ML}. Thus, π-interaction is playing an important role for the lowering of Δ values in all the cases.

TABLE 1—MIXED LIGAND FORMATION CONSTANTS OF SOME HETEROCHELATES OF Zn^{II} AND Cd^{II} AT 30°
Ionic strength, 0.2*M*

Ligand (L)	log $K^{Zn*}_{Zn.L}$	log $K^{Zn.bipy}_{Zn.bipy.L}$ (1 : 1 :1)	log $K^{Cd*}_{Cd.L}$	log $K^{Cd.bipy}_{Cd.bipy.L}$ (1 : 1 : 1)
Glycine	5.22	4.81±0.06	4.24	4.20±0.04
α-Alanine	5.17	4.54±0.04	4.27	4.05±0.02
Leucine	4.74	4.48±0.05	3.92	3.93±0.04
Valine	4.74	4.69±0.06	3.91	3.81±0.04
Serine	5.06	4.79±0.03	3.95	3.76±0.05
Threonine	5.16	4.89±0.06	4.02	3.86±0.02
Methionine	4.69	4.59±0.04	4.30	3.89±0.03

* M. V. Chidambaram, Ph.D. Thesis, M. S. University, Baroda, 1971; J. D. Joshi, Ph.D. Thesis, M. S. University, Baroda, 1974.

Acknowledgement

The author is very thankful to Prof. P. K. Bhattacharya, Science Faculty, M. S. University, Baroda for invaluable suggestions.

References

1. M. V. CHIDAMBARAM and P. K. BHATTACHARYA, *J. Inorg. Nucl. Chem.*, 1970, 32, 3271.
2. H. M. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1954, 2904.
3. G. ADEREGG, *Chim. Acta*, 1963, 46, 2397.
4. G. A. ATKINSON and J. E. BAUMAN, *J. Inorg. Nucl. Chem.*, 1962, 1, 900.
5. I. P. MAVANI, C. R. JEJURKAR and P. K. BHATTACHARYA *J. Indian Chem. Soc.*, 1972, 49, 469.
6. S. N. DUBEY and R. C. MEHROTRA, *J. Indian Chem. Soc.*, 1970, 47, 881.
7. R. GRIESSER, B. PRIJA and H. SIGEL, *Inorg. Nucl. Chem. Lett.*, 1968, 4, 443.

Stabilisation of Molybdenyl Cation(V) in Diverse Anionic Environment by 2(2′-Pyridyl) benzimidazole

H. K. SAHA, (Miss) ANIMA SAHA and S. S. MANDAL

Department of Pure Chemistry, University College of Science, Calcutta-700 009

Manuscript received 23 November 1983, revised 4 July 1984, accepted 20 September 1984

WE have reported in details[1-2] the chemistry of MoO^{3+} in the environment of some diverse anions. The present communication deals with the isolation and study of some oxomolybdenum(V)chloro complexes with 2(2′-pyridyl) benzimidazole (Pybmz) in spin-free state.

Experimental

The ligand was prepared following the standard procedure[5] and the other reagents used were of A.R. grade. Molybdenum and chloride were estimated gravimetrically as molybdenum trioxide and silver chloride. Nitrogen was estimated by Dumas' method. The oxidation state of the metal was determined by ceric sulphate method.

2(2′-Pyridyl) benzimidazoliniumoxopentachloromolybdate(V), $PybmzH_2$ [$MoOCl_5$] :

Molybdenum trioxide (~1 g) was dissolved in HCl (10 ml, 12 *M*) with stirring followed by addition of hydriodic acid (1 ml). The solution was boiled to drive off the liberated iodine. The concentrated small mass was taken up with minimum quantity of conc.HCl when a bright green solution was obtained. To this solution containing $MoOCl_5^{2-}$, was added with stirring a solution of 0.8 g ligand in minimum quantity of HCl when a greenish yellow precipitate was obtained. The precipitate was filtered and dried *in vacuo* over solid KOH to yield the product (1.9 g).

Oxotrichloro [2 (2′-pyridyl)benzimidazole]molybdenum(V), [$MoOCl_3$.Pybmz], (pink) : A sample of the parent salt, $PybmzH_2$ [$MoOCl_5$] (~1 g) was refluxed with dehydrated ethanol (15 ml) for 0.5 h. The pink coloured crystalline solid so formed was filtered and dried in vacuum desiccator to yield the product (0.75 g).

Oxotrichloro [2 (2′-pyridyl)benzimidazole]molybdenum(V), [$MoOCl_3$ (Pybmz)], (orange) : The orange coloured crystalline compound was obtained by refluxing 1g of the original salt (1g) with acetonitrile (15 ml) for 2 h. The solid mass was filtered, washed with acetonitrile and dried *in vacuo* to yield the product (0.73 g).

Alternatively, the orange compound was also prepared by refluxing the parent salt with acetylacetone for 2.5 h. Analytical data of the complexes are given in Table 1.

Results and Discussion

The extensive hydrolysis and ionisation of oxopentahalomolybdate(V) ion was confirmed by conductance measurement of the salt in aqueous medium. The non-electrolytic nature of [$MoOCl_3$. Pybmz] compound was established by conductance measurement in acetonitrile. The conductance values in $10^{-3}M$ solution of the pink and the orange forms are 11.73 and 11.28, 11.68 Ω^{-1} cm^2 mol^{-1}, respectively which are much less than those for binary electrolytes[4].

The μ_{eff} values of the complexes, $PybmzH_2$ [$MoOCl_5$], [$MoOCl_3$.Pybmz] (pink) and [$MoOCl_3$. Pybmz] (orange, two product) are 1.51, 1.62, 1.53

TABLE 1—ANALYTICAL, OXIDATION STATE, MAGNETIC AND CONDUCTANCE DATA FOR OXOMOLYBDENUM(V) COMPLEXES

Compound	Colour	Analysis % : Found/(Calcd.)			Oxidation state	μ_{eff} B.M.	Molar conductance Ω^{-1}
		Mo	Cl	N			
$PybmzH_2$[$MoOCl_5$]	Greenish yellow	20.32 (19.72)	35.69 (36.48)	9.43 (8.68)	5.07	1.513	—
[$MoOCl_3$.Pybmz]	Pink	23.82 (23.23)	25.72 (25.78)	10.56 (10.16)	4.89	1.62	11.73
[$MoOCl_3$.Pybmz]	Orange	23.74 (23.23)	25.87 (25.78)	10.76 (10.16)	4.88	1.53	11.28
[$MoOCl_3$.Pybmz] (from acetylacetone)	Orange	23.73 (23.23)	25.80 (25.78)	9.91 (10.16)	4.91	1.46	11.68

and 1.46 B.M., respectively (Table 1). It appears from the result that the salt and both the varieties of mononuclear complex contain quinquevalent molybdenum having d^1 configurations. The ir spectrum of the salt, PymbzH$_2$ [MoOCl$_5$] shows a strong band at 980 cm^{-1} while for both the varieties of non-electrolyte it appears at 975 cm^{-1}. These bands can be assigned to the terminal Mo=O vibration[5]. The lowering of stretching frequencies by 5 cm^{-1}, from salt to non-electrolyte, may probably be due to the strong donating capabilities of the nitrogen atom of the ligand and thus causing increased electron density around the central metal atom and reducing its π-acceptance capacity and ultimately the metal oxygen bond strength.

The uv and visible spectra of the salt were recorded in 12 *M* HCl while for the other in acetonitrile medium. The observed results clearly agree with the previous observation[6,7].

The salt, 2(2'-pyridyl) benzimidazoliniumoxopentachloromolybdate(V) in 12 *M* HCl shows two crystal field transitions around 14000 ($^2B_2 \rightarrow {}^2E(I)$) and 22000 cm^{-1} ($^2B_2 \rightarrow {}^2B_1$), and three charge transfer transitions around 27000 ($^2B_2 \rightarrow {}^2E(II)$), 34000 ($^2B_2 \rightarrow {}^2B_2(I)$) and 43000 cm^{-1} ($^2B_2 \rightarrow {}^2E(III)$), respectively. Similarly, for both the varieties of non-electrolyte the bands appear around 13000, 19000, 27000, 33000 and 42000 cm^{-1} which may be assigned to the transitions, $^2B_2 \rightarrow {}^2E(I)$, L$\rightarrow$Mo charge transfer, $^2B_2 \rightarrow {}^2B_1$, $^2B_2 \rightarrow {}^2B_2(I)$ and $^2B_2 \rightarrow {}^2E(III)$, respectively.

References

1. H. K. SAHA, B. K. SIKDAR and T. K. RAY CHAUDHURI, *J. Indian Chem. Soc.*, 1982, 59, 723.
2. H. K. SAHA, S. S. MANDAL and P. C. GHORAI, *J. Indian Chem. Soc.*, 1982, 59, 1124.
3. T. R. HARKINS, J. L. WALTER, O. E. HARRIS and H. FREISER, *J. Am. Chem. Soc.*, 1956, 78, 260; T. J. LANE, J. NAKAGAWA, J. L. WALTER and A. J. CANDATHIL, *Inorg. Chem.*. 1962, 1, 267.
4. W. J. GEARY, *Coord. Chem. Rev.*, 1977, 7, 110.
5. K. FREEMAN and G. W. A. FOWLES, *J. Chem. Soc.*, 1965, 4, 310.
6. C. J. BALLHAUSEN and H. B. GRAY, *Inorg. Chem.*, 1962, 1, 111.
7. H. K. SAHA and A. K. BANERJEE, *J. Inorg. Nucl. Chem.*, 1972, 34, 1861.

Oxovanadium(IV) and Dioxouranium(VI) Complexes with Dioxime of Fluorene Glyoxal

U. K. SRIVASTAVA, B. S. YADAV and D. R. SINGH

Chemical Research Laboratory, R. B. S. College, Agra-282 002

Manuscript received 2 May 1983, revised 17 February 1984, accepted 30 May 1984

Of many oxo metal species studied, VO^{2+} and UO_2^{2+} are the most stable[1,2]. Both the ions form various types of stable complexes with different ligands. The complexes of VO^{2+} with macrocyclic ligands[3] derived from 2,6-dipicolinoyldihydrazine and β-diketones have been studied. The electron spin resonance studies on dihalogenovanadium(IV) having different ground states are some recent revelations[4].

The complexes of dioxouranium(VI) with many monobasic bidentate and dibasic tetradentate Schiff bases have been studied recently[5] and many interesting features pertaining to their physico-chemical aspects have been divulged. Aforesaid investigations led to synthesise a new ligand and its complexes with oxovanadium(IV) and dioxouranium(VI) ions. In the present investigation we have isolated oxovanadium(IV) and dioxouranium(VI) complexes of fluorene glyoxal dioxime and characterised them with the help of elemental analysis, magnetic moment, ir and electronic spectral data.

Experimental

All the reagents used were of A.R. grade and the solvents were purified by distillation.

Preparation of ligand: Fluorene glyoxal was obtained from fluorene by its acetylation and subsequent oxidation by selenium dioxide[6].

Dioxime of fluorene glyoxal was prepared by refluxing hydroxylamine hydrochloride and fluorene glyoxal in molar ratio of 2 : 1 in an aqueous NaOH solution for about 30 min. After cooling in ice-bath, 2-3 ml of water was added to get brownish black precipitate. After washing with water it was recrystallised from petroleum ether (b.p. 160°).

Preparation of complexes: Oxovanadyl(IV) complex was prepared by refluxing aqueous ethanolic solutions of vanadyl chloride and ligand in molar ratio of 1 : 2. The green precipitate thus obtained was filtered and washed with aqueous ethanol and finally dried at 120°.

Dioxouranium(VI) complex was prepared by mixing ethanolic solution of dioxime with uranyl iodide solution in ethanol. Uranyl iodide was prepared by methathesis (addition of KI to uranyl acetate). The yellow crystalline complex separated out was filtered, washed with ethanol and dried.

Infrared spectra (KBr) were recorded on Beckman and Unicam SP 1200 spectrophotometer at Department of Chemistry, Delhi University, and Textile and Chemistry Department, I.I.T., New Delhi. The magnetic measurements were carried out at room temperature on Gouy balance. Electronic spectra in solution were recorded on Bausch and Lomb Spectronic-20 spectrophotometer. Carbon and hydrogen were estimated by microanalytical methods. Nitrogen was determined by Kjeldahl's method, vanadium and uranium by conventional gravimetric methods (Table 1).

Results and Discussion

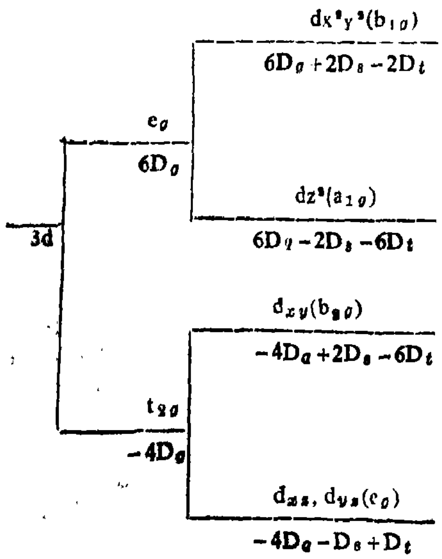
The ligand was found to be brownish black in colour and stable. It showed bidentate nature in all the complexes. In oxovanadium(IV) complex

TABLE 1—ELEMENTAL ANALYSIS OF LIGAND AND OXOVANADIUM(IV) AND DIOXOURANIUM(VI) COMPLEXES

Compound	Colour	Analysis % : Found/(Calcd.)				
		Metal	C	H	N	I
$(C_{15}H_{13}N_3O_3)$	Brownish black	—	66.50 (64.86)	5.50 (5.41)	19.21 (18.61)	—
$[VO(C_{15}H_{11}N_3O_3)H_2O]$	Green	8.34 (8.68)	62.89 (61.32)	3.81 (4.08)	9.34 (9.54)	—
$[UO_2(C_{15}H_{13}N_3O_3)I_2]$	Dark yellow	22.20 (23.19)	35.89 (35.08)	2.09 (2.14)	5.33 (5.45)	24.19 (24.75)

the ligand is deprotonated and in dioxouranium(VI) complex no deprotonation of ligand takes place. Complexes are stable in air and are formed in 1 : 2 metal ligand stoichiometry.

The normal temperature magnetic moment value of oxovanadium(IV) complex lies in the range 1.73-1.75 B.M. while the complex of dioxouranium(VI) shows diamagnetic nature. In d^1 oxovanadium(IV) complex orbital contribution is almost quenched and the spin orbital coupling constant is positive, therefore, the complex exhibits magnetic moment around 1.75 B.M.[1,7], which is well in the range of oxovanadium(IV) complex having symmetry lower than octahedral. This value also suggests that there is no significant antiferromagnetic interactions between pairs of oxovanadium(IV) ions in the complex in solid state. The oxovanadium complex exhibits d-d bands at around 12500, 17600 and 22300 cm^{-1}, possibly due to transitions[9,10] $d_{xy} \rightarrow d_{yz}, d_{xz}$; $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$, indicating destorted octahedrol geometry, elongation being xy plane. But in the present case, the distinction made between axial and equatorial parameters Ds and Dt, respectively indicates the difference in bond length of axial and equatorial bond lengths. The evaluation of these parameters suggests elongation along z-axis, hence, the energy level scheme suggested by Selbin cannot be applied. The scheme proposed by Lever[9] very well explains such distortion.



$(O_h \rightarrow D_{4h})$

Therefore, the observed transitions may be assigned as :

$$125000\ \text{cm}^{-1}\ \nu\ [e_g \rightarrow b_{2g}] \quad (1)$$

$$17600\ \text{cm}^{-1}\ \nu\ [e_g \rightarrow a_{1g}] \quad (2)$$

$$22300\ \text{cm}^{-1}\ \nu\ [e_g \rightarrow b_{1g}] \quad (3)$$

The magnetic and electronic spectral findings on complexes $[VO(L)H_2O]$ of tetradentate macroligands derived from 2,6-dipicolinoyldihydrazine and β-diketones have also been reported recently which lend enough support to our interpretations[8].

Analogous to many dioxouranium(VI) complexes[5] of bidentate and tetradentate Schiff base, $[UO_2X_2(L_2)]$ and $[UO_2X_2L]$, respectively, the present complex has been found to have $[UO_2(C_{15}H_{13}N_3O_3)_2I_2]$ composition. Conductivity measurements indicate that the complex is non-electrolyte. The magnetic measurements show that the complex is diamagnetic. It shows electronic spectral band at 23000 cm^{-1} suggesting the equatorial ligation as it has influenced the spectrum of uranyl ion. This band is assigned to charge transfer $E_g^{1+} \rightarrow {}^3v$, and is lower in range than free uranyl ion[10].

In the dioxouranium(VI) complex, the ir frequency at 320 cm^{-1} is assigned to U—I band[11]. The metal-nitrogen bands have been reported to occur in the region 600-500 cm^{-1} for a number of complexes[12]. An intense band in the region 560-530 cm^{-1} is assigned to M—N vibrations in the present complexes. The ir spectrum of ligand under study shows bands at 3500 (NOH), 1630 (C=N) and 1240 cm^{-1} (N—O) stretchings. The position of N—O band shifts to higher frequency suggesting coordination through nitrogen atoms of dioxime, however, an insignificant change in $\nu_{C=N}$ in the complex is probably on account of strong force existing in C=N group. Similar observations have been made by other workers[13].

In the oxovanadium(IV) complex, the loss of water, relatively at higher temperature (> 150°) indicates that water is coordinated and not lattice-held.

Acknowledgement

The help and facilities made available by Dr. H. B. Singh, Head of Department of Chemistry are thankfully acknowledged. One of the authors (U.K.S.) is also thankful to U.G.C., New Delhi for providing Teacher Fellowship.

References

1. J. Selbin, *Chem. Rev.*, 1965, 65, 153.
2. J. Selbin, *Coord. Chem. Rev.*, 1966, 1, 293.
3. S. Ksher, S. K. Sahini, V. Kumari and R. N. Kapoor, *Inorg. Chim. Acta*, 1979, 37, 121.
4. A. Jezierski and J. B. Raynor, *Inorg. Chim. Acta*, 1980, 44, 153.
5. W. I. Azeez and A. F. Kazeer, *Inorg. Chim. Acta*, 1979, 36, 205.
6. G. C. Saxena, Ph.D. Thesis, Agra University, 1976.
7. A Syamal, *Coord. Chem. Rev.*, 1975, 16, 309.
8. J. Selbin and T. R. Ortolano, *J. Inorg. Nucl. Chem.*, 1964, 26, 1253.
9. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amasterdam, 1971.
10. J. T. Bell, *J. Inorg. Nucl. Chem.*, 1969, 31, 703.
11. J. A. Day and L. M. Venanzi, *J. Chem. Soc.(A)*, 1966, 1363.
12. D. M. Adam, "Metal Ligand and Related Vibrations", Ernold, London, 1967.
13. N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem.*, 1971, 33, 3781.

Metal Derivatives of Antimony Thiocarboxylates. Part-IV. Complexes of Silver(I), Aluminium(III), Chromium(III), Iron(III), O-Zirconium(IV) and Thorium(IV) with Antimony Hydrogen Bis(thiolactate)

SNEH LATA, HEMANT K. SHARMA, S. N. DUBEY
and
D. M. PURI*

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

Manuscript received 26 April 1983, revised 2 May 1984, accepted 20 September 1984

IN continuation to our studies on metal derivatives of antimony hydrogen bis-(thioglycollate) and -(thiolactate)[1,2] we report here the syntheses and structural studies of the complexes of antimony hydrogen bis(thiolactate) with Ag^{I}, Al^{III}, Cr^{III}, Fe^{III}, OZr^{IV} and Th^{IV}. Formation constant studies of Al^{III} and Cr^{III} complexes in aqueous medium have also been made.

Experimental

Materials : All the chemicals used were chemically pure. The ligand, antimony hydrogen bis-(thiolactate) was prepared and purified by known methods[3,4].

Aluminium(III), chromium(III) and iron(III) sulphates (Merck, Pure), Ag^{I}, Zr^{IV} and Th^{IV} nitrates (B.D.H., Pure) solutions were used after analysis.

Preparation of complexes : To a solution of the ligand antimony hydrogen bis(tholactate) in hot water, the required amount of aqueous metal ion solution was added depending upon the ratio in which the reaction was to be carried out. An immediate precipitation of the complex occurred except for aluminium and chromium. The reaction mixture was allowed to stand for some time for complete precipitation. The solid product was then filtered, washed with hot water and hot ethanol, and dried under reduced pressure (2 mm) at 50°.

In case of aluminium and chromium complexes, the precipitation was carried out by adding NaOH solution (0.1 *N*) Metals in the compounds were estimated by the known methods and the results are given in Table 1 along with other data.

TABLE 1—ANALYTICAL DATA OF COMPLEXES

Complex	Colour	Analysis % : Found/(Calcd.) Metal	C	H
$Ag(C_6H_9O_4S_2Sb)$	White	23.86 (24.65)	15.82 (16.45)	1.78 (1.83)
$Al(C_6H_9O_4S_2Sb)_3$	White	2.31 (2.65)	20.04 (21.25)	2.24 (2.36)
$Cr(C_6H_9O_4S_2Sb)_3$	Bluish green	4.62 (5.00)	20.12 (20.74)	2.18 (2.30)
$Fe(C_6H_9O_4S_2Sb)_3$	Dark brown	5.02 (5.34)	20.21 (20.66)	2.38 (2.30)
$OZr(C_6H_9O_4S_2Sb)_2$	White	11.42 (11.90)	18.41 (18.78)	2.01 (2.09)
$Th(C_6H_9O_4S_2Sb)_4$	White	14.10 (14.96)	17.93 (18.57)	1.94 (2.06)

Physical measurements : Ir spectra (nujol) were recorded on Beckman IR-20 spectrophotometer. Magnetic susceptibility measurements were carried out on Gouy balance. The diffused reflectance spectra were recorded on SP700 spectrophotometer. *p*H was measured with a Philips PR 9405M *p*H meter with glass and calomel electrodes assembly. The instrument was calibrated using buffer tablets of *p*H 4 and 9.2.

Results and Discussion

The ligand, antimony hydrogen bis(thiolactate) was prepared as reported earlier[3-4].

In the ir spectrum of thioacetic acid the carbonyl stretching vibrations (ν_{as} and ν_s) were observed at 1715 and 1680 cm^{-1}. These bands shifted to 1625 and 1450 cm^{-1}, respectively on the formation of organoantimony compounds, which further shifted to lower frequency in the ranges of 1570-1550 and 1400-1370 cm^{-1} on complex formation with different metals as observed in their ir spectra. These lowerings suggest that COO^- acted as a bidentate bridging chelating ligand[6] and is consistent with the results obtained in case of $CaCu(OAc)_4.6H_2O$[7]. The zirconium complex showed a sharp band at 870 cm^{-1} (Zr—O)[8].

Magnetic moments of Cr^{III} complex (4.14 B.M.) was consistent with the octahedral structure having d^3 system[1], whereas electronic spectrum of Cr^{III} complex showed bands at 700, 490 and 380 nm as expected for octahedral coordination[9].

The trivalent iron complex was found to have magnetic moment of 3.68 B.M., a value less than that

required for d^5 system, suggesting spin-spin coupling between unpaired electrons of neighbouring iron atoms[10,11]. The bands at 700, 590 and 350 nm observed in the electronic spectrum of Fe^{III} complex could be attributed[19] to the transitions $^4T_{1g}(4_G) \rightarrow {}^6A_{1g}$, $^4T_{2g}(4_G) \leftarrow {}^6A_{1g}$ and $^4T_{2g}(4_D) \leftarrow {}^6A_{1g}$

Other complexes were found to be diamagnetic as was expected.

Thus, analytical data, high m.p., insolubility in different organic solvents and water, magnetic moment values, ir and electronic spectral data suggest these complexes to be polymeric in nature.

Formation constants of Al^{III} and Cr^{III} complexes: The dissociation constant of the ligand antimony hydrogen bis(thiolactate) was determined by the differential method[18] and the value was found to be 3.162×10^{-6}.

Metal-ligand formation curves were obtained by plotting the values $\bar{n}$ *vs* pL and stepwise formation constants, log K_n, were determined using the following techniques[14,15], (i) interpolation of half $\bar{n}$ values, (ii) pointwise calculation method, and (iii) curve-fitting method.

The final values of log K_1, log K_2 and log K_3 for Al^{III} and Cr^{III} complexes were found to be 3.79, 3.23, 2.86, and 4.05, 3.52, 2.84, respectively.

The formation constants of the other metal ion complexes could not be determined due to immediate precipitation of the complex on titration.

Acknowledgement

The authors gratefully thank Prof. V. Yatirajam, Chairman, Department of Chemistry, Kurukshetra University for providing facilities. Two of the authors (S.L. and H.K.S.) are also thankful to C.S.I.R., New Delhi for financial help.

References

1. H. K. SHARMA, SNEH LATA, S. N. DUBEY and D. M. PURI, *Indian J. Chem., Sect. A*, 1981, 20, 1031.
2. SNEH LATA, H. K. SHARMA, S. N. DUBEY and D. M. PURI, *J. Indian Chem. Soc*, in the press.
3. P. KLASON and T. CARLSON, *Chem. Ber.*, 1906, 39, 732.
4. L. RAMBERG, *Chem. Ber.*, 1906, 39, 1356.
5. HOLMBERG, *Z. Anorg. Chem.*, 1908, 56, 385.
6. C. A. MCAUTIFFE, J. V. QUAGLIANO and L. M. VALLARINO, *Inorg. Chem.*, 1966, 5, 1906.
7. D. A. LANGE and C. R. HARE, *Chem. Comm.*, 1967, 890.
8. L. N. KOMMISSAROVA, Z. N. PROZOROVSKAYA and V. I. SPITSYN, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1966, 11, 1089.
9. A. B. P. LEVER, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968, p. 308.
10. M. A. ALI, S. E. LIVINGSTON and D. PHILIPS, *Inorg. Chim. Acta*, 1971, 5, 119 ; 1972, 6, 11, 39.
11. M. T. BECK, "Chemistry of Complex Equilibria", Van Nostrand Reinhold, London, 1970.
12. S. K. SENGUPTA, S. K. SAHNI and R. N. KAPOOR, *Indian J. Chem., Sect. A*, 1980, 19, 703.
13. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", E.L.B.S. and Longmans Green, London, 3rd. ed., 1961, 931.
14. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397 ; 1954, 2904.
15. S. N. DUBEY and R. C. MEHROTRA, *Indian J. Chem.*, 1967, 5, 327.

Preparation and Characterisation of Mixed (Ca+Ba+Cu) Hydroxylapatites

PREMA N. PATEL*

Department of Post-Graduate Studies and Research in Applied Chemistry, G. M. College, Sambalpur-768 004

and

O. P. AGRAWAL

Department of Chemistry, Panchayat College, Bargarh, Sambalpur

Manuscript received 16 June 1982, revised 5 March 1984, accepted 20 September 1984

HYDROXYLAPATITE is assigned the formula $Ca_{10}(PO_4)_6(OH)_2$, (CaHA). In recent years, attention has been directed towards all of the basic calcium phosphates for the elucidation of the processes of calcification in general and for dentistry in particular. Hydroxylapatite is now recognised as the most important of the inorganic constituents of human bone and teeth[1,2]. It belongs to an isomorphous series of compounds known as apatites. Apatite undergoes a series of cationic and anionic replacement reactions[3]. $Ca^{2+} \rightarrow Ba^{2+}$ and/or Cu^{2+} replacement reactions in CaHA is of extreme biological significance. They form the basis of incorporation of Ba^{II} and Cu^{II} ions into human skeletal system according to the following equation.

$$Ca_{10}(PO_4)_6(OH)_2 + Ba^{2+} + mCu^{2+} \rightarrow Ca_{9-m}Ba_1Cu_m(PO_4)_6(OH)_2 + (1+m)\,Ca^{2+}$$

Solid solutions of calcium, barium and copper hydroxylapatites were prepared earlier[4] by firing mixtures containing various proportions of calcium, barium and copper hydroxylapatites at about 1300°. These samples prepared by the solid state reaction were, however, found to be discontinuous and non-homogenous.

Now an attempt has been made at a new method of preparation of the homogenous solid solutions of mixed (Ca+Ba+Cu) hydroxylapatites over the entire compositional range by the method of co-precipitation[5-8].

Stoichiometric quantities of ammonium dihydrogen phosphate (Solution A) and a soultion containing Ca^{II}, Ba^{II} and Cu^{II} ions in the proportion desired for the solid solutions (Solution B) were prepared separately in CO_2-free double-distilled water. The pH of the solutions were maintained at ~11. A part of the Solution B was taken in a flask (2l) fitted with two separating funnels and a delivery tube. Solution A and Solution B taken separately in the separating funnels were then added dropwise simultaneously. Precipitation was carried out in CO_2-free atmosphere and the medium was well stirred by bubbling CO_2-free air.

TABLE 1—CHEMICAL ANALYSIS OF $Ca_{10-(n+m)}Ba_nCu_m(PO_4)_6(OH)_2$ (where n = 1)

Sl. no.	Analysis % Ca	Ba	Cu	P	Molecular formula	Mol. vol.	g-atom ratio (Ca+Ba+Cu)/P	Lattice parameter Å a	c	Unit cell vol. $\frac{\sqrt{3}}{2}a^2c$
1.	39.88	—	–	18.50	$Ca_{10}(PO_4)_6(OH)_2$	338.32	1.665	9.37	6.86	523.12
2.	29.52	11.10	5.14	16.70	$Ca_{8.2}Ba_{0.90}Cu_{0.90}(PO_4)_6(OH)_2$	335.25	1.656	9.36	6.85	519.72
3.	25.10	11.43	10.58	16.29	$Ca_{7.15}Ba_{0.95}Cu_{1.90}(PO_4)_6(OH)_2$	333.20	1.664			
4.	20.64	12.27	15.69	15.83	$Ca_{6.05}Ba_{1.05}Cu_{2.9}(PO_4)_6(OH)_2$	324.48	1.662	9.29	6.82	509.74
5.	16.94	11.50	21.01	15.57	$Ca_{5.05}Ba_{1.05}Cu_{3.9}(PO_4)_6(OH)_2$	329.16	1.658			
6.	13.73	12.88	24.11	15.17	$Ca_{4.20}Ba_{1.15}Cu_{4.65}(PO_4)_6(OH)_2$	334.06	1.666			
7.	10.10	12.63	28.97	14.87	$Ca_{3.15}Ba_{1.15}Cu_{5.7}(PO_4)_6(OH)_2$	345.09	1.665	9.16	6.74	489.76
8.	6.64	11.22	34.34	14.67	$Ca_{2.1}Ba_{1.05}Cu_{6.85}(PO_4)_6(OH)_2$	340.12	1.667			
9.	3.41	11.67	38.23	14.36	$Ca_{1.1}Ba_{1.1}Cu_{7.8}(PO_4)_6(OH)_2$	345.05	1.666			
10.	–	9.47	44.28	14.24	$Ba_{0.90}Cu_{9.1}(PO_4)_6(OH)_2$	342.14	1.665	8.98	6.62	462.32
11.	–	–	51.27	51.01	$Cu_{10}(PO_4)_6(OH)_2$	347.68	1.662	8.83	6.53	440.93

The precipitate and mother liquors were aged under reflux for 30 min to improve the homogeneity and crystalinity of the precipitate. The maintenance of the desired *p*H during precipitation was ensured by testing the filtrate after separation of the precipitate, since any alteration of *p*H of the medium during precipitation leads to the formation of calcium deficient apatites[9]. The precipitate was washed thoroughly with double-distilled water to free it from ammonium salts and dried at 100°. The samples were analysed complexometrically and their molar volumes were determined by density method using toluene[10] as a solvent.

The *X*-ray diffraction patterns of the samples were obtained with Siemens powder diffractometer with NaCl (TL) counter employing Cu–K_α (Ni-filtered) radiation, (2 θ) with a scanning speed of 1° min^{-1} using tube voltage and current of 30 kV and 24 mA, respectively. The d-spacing and the corresponding a and c parameter values were calculated by the method of Azaroff[11] and from these unit cell volumes of the samples were determined (Table 1).

The results of chemical analyses of the samples are given in Table 1. Based on the fact that a mole of each sample has a total 10 g-atom of calcium and/or barium and/or copper, the molecular formula of the samples were calculated from the results of the columns 2-4 and included in column 6 of the Table. The g-atom ratios (Ca+Ba+Cu)/P in a mole of each sample was calculated from the results of columns 2-5 and given in column 8 of Table 1. The fact that the observed value of molar g-atom ratios of Ca/P, Ba/P, Cu/P for the end members and (Ca+Ba+Cu)/P were found to be equal to 1.655 (theoretical 1.67) is consistent with the formation of homogeneous solid solution[10]. This was further supported by the closeness of the values of molar volumes of the end members and those of the intermediate samples which lie within the range of end members.

The formation of solid solutions can be further confirmed by *X*-ray diffraction analysis. It is well established that all the members of the apatite series exhibit hexagonal crystals, belonging to hexagonal-bipyramidal class, 6/m (space group $P6_{3/m}$)[12,13]. Lattice parameter showed unit cell dilation and contraction consequent upon the introduction of bigger Ba^{II} ion (1.35 Å) and smaller Cu^{II} ion (0.72 Å), respectively in place of Ca^{II} ion (0.99 Å) in the apatite lattice.

Acknowledgement

Authors thank Dr. G. Ferraris, Professor of Crystallography, University of Torino, Italy for *X*-ray data and Prof. T. Kabi, Ex-Principal, G. M. College, Sambalpur for encouragement and facilities.

References

1. W. F. NEUMAN and M. W. NEUMAN, *Chem. Rev.*, 1953, **53**, 1.
2. R. A. ROBINSON, *J. Bone Joint Surg.*, 1962, **34**, 389.
3. J. R. VANWAZER, "Phosphorus and Its Compounds", Interscience, New York, Vol. 2, p. 530.
4. J. R. VAN WAZER, "Phosphorus and Its Compounds", Interscience, New York, 1966, Vol. 2, p. 1429.
5. P. N. PATEL, *Chem. Ind. (London)*, 1978, **21**, 804.
6. P. N. PATEL, *J. Indian Chem. Soc.*, 1979, **56**, 410.
7. P. N. PATEL, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1129.
8. P. N. PATEL, *Chem. Ind. (London)*, 1980, **19**, 14.
9. E. E. BERRY, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1585.
10. J. R. PARTINGTON, "An Advanced Treatise on Physical Chemistry", Longman Green, London, 1952, Vol. 3, p. 121.
11. L. V. AZAROFF, "Elements of *X*-ray Crystallography", McGraw-Hill, London, 1968, Chapter 13.
12. M. MEHMEL *Z. Krist.*, 1930, **75**, 323 ; ST. NARAY-SZABO, *Z. Krist.*, 1930, **75**, 387.
13. H. WENT SCHEL, *Zentralbl. Mineral Geol.*, 1923, **609**.

Oxidation of Diketones. Vanadium(V) Oxidation of Acetyl Acetone and Benzoyl Acetone†

(Miss) D. SHRIVASTAVA

Janta College, Rewa

and

V. K. SHARMA and (Mrs.) K. SHARMA*

Department of Chemistry, Government Science College, Rewa-486 001

Manuscript received 17 January 1984, revised 16 June 1984, accepted 20 September 1984

In continuation to our earlier report on oxidation of compounds containing active methylene group by vanadium(V) in acid medium[1], the oxidation kinetics of acetyl and benzoyl acetones in sulphuric acid are further extended in the present communication.

Experimental

Ammonium metavanadate (Reidel) was dissolved in appropriate concentration of sulphuric acid (B.D.H., A.R.) to prepare vanadium(V) solution. The ketones were purified by distillation and their solutions were used in glacial acetic acid. Other chemicals employed were of AnalaR grade.

Adequate concentrations of the reactants were mixed and the rate of oxidation was followed by estimating the unconsumed V^V in aliquotes withdrawn at regular intervals by titrating against ferrous ammonium sulphate solution using *N*-phenylanthranilic acid as an indicator.

Results and Discussion

Kinetic studies were arranged under the conditions $[H_2SO_4]$ and [ketone] $\gg [V^V]$ at constant ionic strength. The results can be summarised as follow :

(i) The reactions are first order in V^V as the plots of log (a-x) *vs* time are linear. Moreover, the first order rate constants for different initial concentrations of V^V for a particular [ketone] and $[H^+]$ are almost the same proving the first order dependence in V^V (Tables 1 and 2).

(ii) The pseudo first order rate constant increases with increase in [ketone]. The plots of log k_1 *vs* log [ketone] are linear with slopes nearly unity (acetyl acetone =1.12, and benzoyl acetone =1.01) and also the constancy in second order rate constants (k_2), thereby indicating that the order is one in ketones. A positive intercept on the Y-axis of the plots between k_1^{-1} and $[ketone]^{-1}$ gives an evidence of complex formation between V^V and ketones. Similar observations have been reported[1,2] in the oxidation of other ketones by V^V.

(iii) Concentration of H_2SO_4 was varied to study the effect of $[H^+]$ on the rates of the reactions (Tables 1 and 2). The plots of log k_1 *vs* log $[H^+]$ are linear with slopes 1.13 and 1.16 for acetyl acetone and benzoyl acetone, respectively. Hammett plots of log k_1 *vs* H_0 are linear with slopes less than unity (acetyl acetone =0.41, benzoyl acetone=0.45) which are comparable to those reported for the oxidation of methyl ethyl ketone[3] and citric acid[3].

(iv) The effect of change in dielectric constant of the medium by changing the percentage-composition of acetic acid in solvent mixture shows a decrease in the rate of oxidation. The linear plots between log k_1 and 1/D with positive slopes suggest the reactions to be of ion-dipole type. Addition of $NaHSO_4$ increases the rate, whereas Na_2SO_4 decreases it.

TABLE 1—DEPENDENCE OF RATE ON REACTANTS AT 50°

[HOAc] = 40% (v/v)

$[V^V]$ $\times 10^{3} M$	[AA] $\times 10^{2} M$	$[H^+]$ M	μ M	k_1 $\times 10^{3}$ min^{-1}	$k_2 \times 10^{2}$ l mol^{-1} min^{-1}
2.50	10.00	2.0	2.01	12.40	–
4.00	10.00	2.0	2.01	11.70	–
5.00	10.00	2.0	2.01	11.76	–
6.66	10.00	2.0	2.01	11.77	1.17
10.00	10.00	2.0	2.01	12.18	–
6.66	5.00	2.0	2.01	6.37	1.27
6.66	6.00	2.0	2.01	8.36	1.26
6.66	13.30	2.0	2.01	17.37	1.30
6.66	20.00	2.0	2.01	25.25	1.26
6.66	25.00	2.0	2.01	32.05	1.28
6.66	10.00	1.5	3.51	17.21	1.14
6.66	10.00	2.0	3.51	22.24	1.11
6.66	10.00	2.5	3.51	28.12	1.12
6.66	10.00	3.0	3.51	34.21	1.14
6.66	10.00	3.5	3.51	40.02	1.14

AA = Acetyl acetone.

TABLE 2—DEPENDENCE OF RATE ON REACTANTS AT 50°

[HOAc] = 43.3% (v/v)

$[V^V]$ $\times 10^{3} M$	[BA] $\times 10^{2} M$	$[H^+]$ M	μ M	k_1 $\times 10^{3}$ min^{-1}	$k_2 \times 10^{2}$ l mol^{-1} min^{-1}
2.50	3.33	3.0	3.01	13.32	–
3.33	3.33	3.0	3.01	13.37	4.00
4.00	3.33	3.0	3.01	13.94	–
5.00	3.33	3.0	3.01	13.90	–
10.00	3.33	3.0	3.01	14.29	–
3.33	0.50	3.0	3.01	2.00	4.00
3.33	1.00	3.0	3.01	3.95	3.95
3.33	2.00	3.0	3.01	7.36	3.68
3.33	2.50	3.0	3.01	9.53	3.81
3.33	4.00	3.0	3.01	15.92	3.98
3.33	3.33	2.5	4.51	25.11	1.00
3.33	3.33	3.0	4.51	35.92	1.19
3.33	3.33	3.5	4.51	42.91	1.21
3.33	3.33	4.0	4.51	47.51	1.18
3.33	3.33	4.5	4.51	56.23	1.24

BA = Benzoyl acetone.

† Abstracted in the Proceedings 71st. Session of the Indian Science Congress.

* 20/5, Kothi Road, Rewa-486 001.

Mechanism : The parent species of V^V in mineral acids is considered[4] to be VO_2^+. At slightly higher acid concentration VO_2^+ is assumed to be in equilibrium with $V(OH)_3^{2+}$ (equation 1)

$$VO_2^+ + H_2O + H^+ \overset{K_1}{\rightleftharpoons} V(OH)_3^{2+} \quad (1)$$

The marked colour of sulphuric acid solution of V^V suggests that one HSO_4^- may be incorporated in the active species[5-7] which may be represented as $V(OH)_3HSO_4^+$ (equation 2). The effect of the addition of $NaHSO_4$ and Na_2SO_4 lends support to the equilibrium,

$$VO_2^+ + H_2SO_4 + H_2O \overset{K_1'}{\rightleftharpoons} V(OH)_3HSO_4^+ \quad (2)$$

Polymerisation test with acrylonitrile is positive, indicating the formation of free radical intermediates and also that V^V acts as one-electron oxidant.

The experimental results, therefore, lead to the following rate expression.

$$V(OH)_3HSO_4^+ + \text{ketone} \overset{K_2}{\rightleftharpoons} \text{complex} \quad (3)$$

$$\text{complex} \xrightarrow[\text{slow}]{k_1} R\dot{C}HCOCH_3 + V(OH)_2^{2+} \quad (4)$$

$$R\dot{C}HCOCH_3 + 4V^{5+} + 3H_2O \xrightarrow{\text{fast}} \dot{R} + CH_3COOH + HCOOH + 4V^{4+} + 4H^+ \quad (5)$$

$$\dot{R} + V^{5+} + H_2O \xrightarrow{\text{fast}} CH_3COOH \text{ or } C_6H_5COOH + V^{4+} + H^+ \quad (6)$$

At constant $[V^V]_T$

$$k_{obs} = \frac{K_1' K_2\, k_1\, [\text{ketone}]\, [H_2SO_4]}{1 + K_1'\, [H_2SO_4] + K_1' K_2\, [\text{ketone}]\, [H_2SO_4]} \quad (7)$$

According to Wells and Kuritsyn[8], the equilibrium constant for the formation of $V(OH)_3^{2+}$ is much less than one. Therefore, it can be assumed that K_1' is very small as compared to $K_2 k_1$.

$$\frac{1}{k_{obs}} = \frac{1}{X\,[\text{ketone}]} + \frac{1}{k_1} \quad (8)$$

where $X = K_1' K_2 k_1 [H_2SO_4]$ at constant concentration of H_2SO_4. The plots of $1/k_{obs}$ *vs* 1/[ketone] are linear with positive intercept on Y-axis.

Since K_1' is less than unity, $K_1' K_2$ is also less than one and hence, the equation (7) may be expressed as

$$k_{obs} = k_1 K_1' K_2\, [\text{ketone}]\, [H_2SO_4] \quad (9)$$

and at constant concentration of sulphuric acid

$$k_{obs} = K'\, [\text{ketone}]$$

where, $K' = K_1' K_2 k_1 [H_2SO_4]$.

The plots of k_{obs} *vs* [ketone] should be linear passing through the origin.

Values of entropy of activation too confirm the C–H fission in the mechanistic steps. Kinetic results show that the reactivity of benzoyl acetone is more than acetyl acetone. This may be due to the conjugation effect.

Acknowledgement

One of the authors (D.S.) wishes to thank U.G.C., New Delhi for financial assistance. The authors are grateful to Dr. D. S. Dakwale for facilities.

References

1. D. SHRIVASTAVA, V. K. SHARMA and K. SHARMA, *Vijna Parishad Ansa Patri*, 1983, **26**, 211.
2. PILLAI, G. CHITHAMBARATHANU, J. RAJARAM and J. C. KURIACOSE, *Indian J. Chem., Sect. A*, 1977, **15**, 608 ; 1980, **19**, 589.
3. R. N. MEHROTRA, *J. Chem. Soc. B*, 1968, 1564.
4. F. J. C. ROSSOTTI and H. ROSSOTTI, *Acta Chem. Scand.*, 1956, **10**, 957 ; N. INGRI and F. BRITO, *Acta Chem. Scand.*, 1959, **13**, 1971.
5. W. A. WATERS and J. S. LITLLER, *J. Chem. Soc.*, 1963, 352.
6. S. SUCCUBAI and M. SANTAPPA, *Indian J. Chem.*, 1970, **8**, 533.
7. K. K. SENGUPTA, J. K. CHAKALDAR and B. P. PAL, *J. Chem. Soc., Perkin Trans. 2*, 1973, **7**, 926.
8. G. F. WELLS and L. V. KURITSYN, *J. Chem. Soc. A*, 1970, 1372.

Kinetics of Oxidation of Diphenyl Methane by Selenium Dioxide

N. D. VALECHHA* and (Miss) ASHA PRADHAN

Chemistry Department, Government Science College, Rewa-486 001

Manuscript received 24 January 1984, revised 19 June 1984, accepted 20 September 1984

SELENIUM dioxide has been used as an oxidant in the study of kinetics of oxidation of some ketones[1-4], though similar studies with diphenylmethane have not been made so far. The rate of oxidation of diphenyl methane by chromic acid in glacial acetic acid is extremely rapid at first, but soon slackens and stops almost entirely after a few hours though both diphenylmethane and Cr^{VI} remain in solution[5]. Literature survey shows that much work has been done on the mechanism of oxidation of olefins by selenium dioxide[6-12], but it seems that no attention has been given to the kinetics and mechanism of oxidation of diphenylmethane and related hydrocarbons by selenium dioxide. These have prompted us to study the kinetics of oxidation of diphenylmethane by selenium dioxide to obtain the information on the mechanism of oxidation.

In continuation of our recent interest in the kinetics of oxidation of organic compounds containing active methylene group by selenium dioxide[13-14], we report, in this note, the kinetics of oxidation of diphenylmethane by selenium

dioxide in 80%(v/v) dioxane-water mixture in the presence of perchloric acid (0.30-0.75*M*).

Experimental

Reagents used were selenium dioxide (Loba), diphenylmethane (Sisco), dioxane (B.D.H.), perchloric acid (Riedel), and the other chemicals were of A.R. quality. Stock solution of selenium dioxide was prepared in distilled water and standardised iodometrically. The reactions were studied in thermostat ($\pm 0.1°$). The rate of reaction was determined by estimating the unreacted selenium dioxide iodimetrically[4].

Stoichiometry of the reaction was determined. It was found that one mole of diphenylmethane for complete oxidation required one mole of selenium dioxide.

$$C_6H_5CH_2C_6H_5 + SeO_2 = C_6H_5COC_6H_5 + Se + H_2O$$

The product, benzophenone, was identified by preparing 2,4-dinitrophenylhydrazone, m.p. 237°. Selenium was tested by its characteristic spot test[15].

Results and Discussion

The kinetics of oxidation of diphenylmethane by selenium dioxide has been studied in 80% (v/v) dioxane-water mixture in the presence of perchloric acid. The order of reaction with respect to selenium dioxide is one. The pseudo first order rate constant increases with increase in the concentration of diphenylmethane, however, the value of k/[DPM] remains constant. This clearly indicates that the order with respect to diphenylmethane is unity. The pseudo first order rate constant increases with increase in the concentration of perchloric acid, but the dependence of rate constant on perchloric acid concentration is not simple (Table 1).

TABLE 1—EFFECT OF CONCENTRATION OF REACTANTS AND SOLVENT COMPOSITION ON REACTION RATE

Temp. = 65° Dioxane-water = 4 : 1(v/v)

Effect of selenium dioxide concentration

[Diphenylmethane] = 0.5*M*, $[HClO_4] = 0.5M$

$[SeO_2]M$	0.005	0.010	0.015	0.020
$10^{2}k$ min^{-1}	1.56	1.49	1.47	1.42

Effect of diphenylmethane concentration

[Selenium dioxide] = 0.01*M*, $[HClO_4] = 0.5M$

[DPM]*M*	0.25	0.30	0.40	0.50	0.60
$10^{2}k$ min^{-1}	0.76	0.89	1.18	1.49	1.82
$10^{2}k$/[DPM] l mol^{-1} min^{-1}	3.04	2.96	2.95	2.98	3.03

Effect of perchloric acid concentration

[Selenium dioxide] = 0.01*M*, [Diphenylmethane] = 0.5*M*

$[HClO_4]M$	0.30	0.40	0.50	0.60	0.75
$10^{2}k$ min^{-1}	0.93	1.17	1.49	2.14	2.75

Effect of percentage composition of dioxane

[Selenium dioxide] = 0.01*M*, [Diphenylmethane] = 0.5*M*, $[HClO_4] = 0.5M$

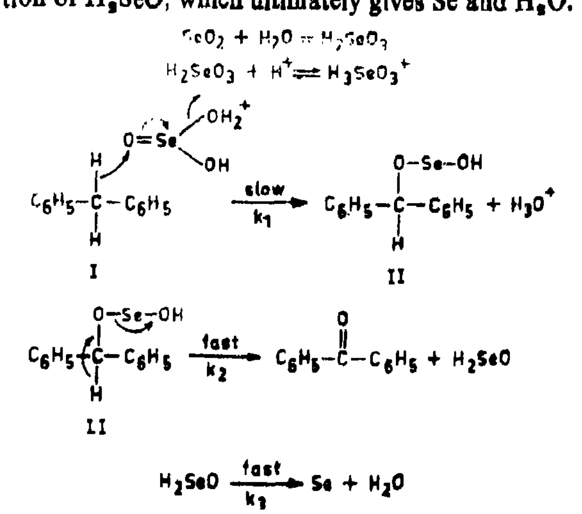
Dioxane-water (v/v)	75-25	80-20	85-15
$10^{2}k$ min^{-1} ($k = k_1/2.303$)	0.73	1.49	3.38

The pseudo first order rate constant in selenium dioxide increases with the decrease in selenium dioxide concentration. It is known[16-17] that selenium(IV) dimerises in aqueous acidic media, so, selenium(IV) will exist both in monomeric and dimeric form in the reaction mixture in the concentration range[18] employed for the present investigation. Thus, the increase in the rate with decreasing concentration of selenium dioxide may be attributed to lower concentration of dimeric selenium(IV), that is, by assuming that as an oxidant the dimer is less reactive than the monomer as in the case of cerium(IV).

The change in ionic strength produced by K_2SO_4 has nearly no effect on the reaction rate, suggesting that at least one of the reacting species involved in the rate determining step is a neutral molecule[19]. The increase in the percentage of dioxane in the reaction mixture largely enhances the reaction rate (Table 1). The plot of log k *vs* percentage composition of dioxane, that is, 1/D is linear having positive slope, suggesting the reaction is a positive ion-dipole[20] type.

The kinetics of oxidation of diphenylmethane by selenium dioxide has been studied at four different temperatures. The plot of log k *vs* 1/T is linear. The activation parameters have been evaluated, using Arrhenius and Eyring's equations. The calculated values of energy of activation (E_a,) frequency factor (A), entropy of activation (ΔS^*) and free energy of activation (ΔG^*) are 15.65 kcal mol^{-1}, 1.51×10^{8} l mol^{-1}sec^{-1}, -35.10 e.u. and 25.95 kcal mol^{-1}, respectively.

Mechanism: Based on the above experimental facts, the proposed reaction mechanism involves an attack of conjugated acid of selenious acid, $H_3SeO_3^+$, at the active methylene group of diphenylmethane (I) in a slow step to give selenium(II) intermediate (II). The latter would yield benzophenone by 1,2-elimination of H_2SeO, which ultimately gives Se and H_2O.



In the present kinetic investigation, it has been observed that under identical experimental conditions, the acid catalysed oxidation of diphenylmethane by selenium dioxide occurs at a measurable

rate in dioxane-water (Table 2), while the oxidation rate, being very slow, is not measurable in acetic acid-water. This indicates that acetic acid is not a good solvent in the selenium dioxide oxidation of diphenylmethane. However, acetic acid has been found to be a good solvent in the selenium dioxide oxidation of olefins[6-12], ketones[1-4,9], ester[14], *etc.*

Unlike chromic acid[5] oxidation of diphenylmethane in glacial acetic acid, the acid catalysed oxidation of diphenylmethane by selenium dioxide in dioxane-water, under the condition $[SeO_2] \ll$ [diphenylmethane], proceeds smoothly till the oxidant is consumed completely (Table 2).

TABLE 2—ACID CATALYSED OXIDATION OF DIPHENYLMETHANE BY SELENIUM DIOXIDE UNDER CONDITION $[SeO_2] \ll [DPM]$ IN 80%(v/v) DIOXANE-WATER

$[SeO_2] = 0.01M$, $[DPM] = 0.5M$, $[HClO_4] = 0.75M$, Temp. = 65°

Time min.	0	30	60	90	120	150
	180	210	240	270	300	330
$[SeO_2]$ in ml of	4.1	3.5	3.0	2.6	2.2	1.8
$Na_2S_2O_3$	1.4	1.1	0.9	0.75	0.6	0.5
$10^4 k$ min^{-1}	–	2.29	2.26	2.22	2.25	2.38
	2.59	2.75	2.74	2.75	2.78	2.76
$(k = k_1/2.303)$						

The temperature coefficient for the present reaction is nearly 2, while relatively small effect of temperature was observed[5] in the chromic acid oxidation of diphenylmethane.

The present kinetic investigation gives information on the mechanism of acid catalysed oxidation of diphenylmethane by selenium dioxide, which has not been reported previously.

Acknowledgement

The authors wish to express gratefulness to Prof. D. S. Dakwale, Head, Chemistry Department for providing facilities.

References

1. F. R. DUKE, *J. Am. Chem. Soc.*, 1948, 70, 419.
2. E. J. COREY and J. P. SCHAEFER, *J. Am. Chem. Soc.*, 1960, 82, 918.
3. J. P. SCHAEFER, *J. Am. Chem. Soc.*, 1962, 84, 713, 717.
4. K. J. SINGH and S. N. ANAND, *J. Indian Chem. Soc.*, 1979, 56, 363.
5. R. SLACK and W. A. WATERS, *J. Chem. Soc.*, 1948, 1666.
6. E. SCHWENK and E. BORGWARDT, *Chem. Ber.*, 1932, 65, 1601.
7. A. GUILLMONAT, *C. B. Hebd. Seances Acad. Sci.*, 1935, 200, 1416.
8. K. B. WIBERG and S. D. NIELSEN, *J. Org. Chem.*, 1964, 29, 3353.
9. J. P. SCHAEFER and B. HORVATH, *Tetrahedron Lett.*, 1964, 30, 2023.
10. D. H. OLSON, *Tetrahedron Lett.*, 1966, 19, 2053.
11. J. P. SCHAEFER, B. HORVATH and H. P. KLEIN, *J. Org. Chem.*, 1968, 33, 2647.
12. E. N. TRACHTENBERG, C. H. NELSON and J. R. CARVER, *J. Org. Chem.*, 1970, 35, 1653.
13. N. D. VALECHHA and A. PRADHAN, *J. Indian Chem. Soc.*, 1984, 61, 495.
14. N. D. VALECHHA and A. PRADHAN, *Indian J. Chem. Sect. A*, communicated.
15. F. FEIGL, "Spot Tests", Elsevier, London, Vol. 1, 1954, p. 341.
16. L. BERCZA and G. SILLEN, *Acta Chem. Scand.*, 1971, 25, 1250.
17. J. N. COOPER, M. WOODS, J. C. SULLIVAN and E. DEUTSCH, *Inorg. Chem.*, 1976, 15, 2862.
18. L. S. A. DIKSHITULU, P. VANI and V. HANUMANTH RAO, *Indian J. Chem., Sect. A*, 1981, 20, 36.
19. J. N. BRONSTED, *J. Physik. Chem.*, 1922, 102, 169.
20. E. S. AMIS. *J. Chem. Educt.*, 1953, 30, 351.

Studies on Resorcinol Formaldehyde Cationic Resins†

J. RAGUNATHAN** and S. KRISHNAMOORTHY*

Department of Chemistry, Regional Engineering College, Tiruchirapalli-620 015

Manuscript received 21 January 1984, revised 26 June 1984, accepted 20 September 1984

SYNTHESIS and study of ion exchangers is of interest because of their large scale use particularly in analytical chemistry and in the softening of water. There is a greater need now either to find out altogether newer resins which are economical compared to the existing exchangers or to identify substitutes which can partly replace the polymeric content of the existing exchangers to a considerable extent while retaining the properties of the parent resins.

Earlier work done has revealed that coke[1], sawdust[2], lignite could be substituted upto 30-40 percent in phenolic cationities. Such a substitution did not have any adverse effect and in addition the composites obtained were macroporous.

In fact, cation exchangers can be made from almost any material which reacts with sulphuric acid without being dissolved, such as the sulphonated olive pits[3], and nut shells and spent coffee[4], tar[5], paper[6], cotton, *etc.*

The present work is an attempt to prepare and study the properties of sulphonated resorcinol formaldehyde cation exchangers substituted partially by sulphonated charcoal obtained from coconut fibre.

Experimental

Preparation of the sample: Reagents used were resorcinol and formaldehyde (B.D.H.), and concentrated H_2SO_4 (sp.gr.1.82). Coconut fibre was procured from local industries and cleaned before use.

Resorcinol (10 g) and conc. H_2SO_4 (12.5 ml) were mixed slowly with constant cooling. Then the

†Presented at the 20th Annual Convention of Chemists, Cuttack, December, 1983.

**Department of Chemistry, H. H. Raja's College, Pudukkottai.

mixture was heated on a water bath for 1 h and polymerised with 37% formaldehyde (12.5 ml). The content were heated for 6 h and the resinous mass was washed free of acid and cured at 70° for several hours.

Sample II was prepared by adding conc. H_2SO_4 to coconut fibre and heated on a water bath for 6 h and then washed it free from acid and dried at 70° overnight. The coconut fibre was thus carbonized and sulphonated. Similarly, samples with 20, 25, 30, 40, 60 and 80% coconut charcoal were prepared by adding 6.5, 8.7, 11.1, 17.3, 26 and 39 g of coconut charcoal to sulphonated resorcinol and polymerised using formaldehyde.

Physical measurements :

(a) *Density* : The density of the resin in both the hydrated and dehydrated states was obtained with the aid of a specific gravity bottle, in water and in toluene, respectively.

(b) *Particle size* : Particle size was determined by sieving the samples through 200 mesh.

TABLE 1—AMOUNTS OF REAGENTS USED AND YIELDS OF COMPOSITES

Sample	Weight of reagent taken, g		Amount of coconut charcoal added	Yield	Coconut charcoal in resin
	Resorcinol	Formaldehyde	g	g	%
A	10	12.5	0	26	0
B	10	12.5	6.5	30.8	20
C	10	12.5	8.7	34.0	25
D	10	12.5	11.1	36.4	30
E	10	12.5	17.3	42.1	40
F	10	12.5	26.0	51.1	60
G	10	12.5	39.0	62.9	80

(c) *Attrition effect* : Attrition effect on the samples were compared with that of the unsubstituted resin as follows. Both types of the samples were initially sieved to give batches containing particles greater than 200 mesh size. They were swollen in water and shaken continuously for 6 h. Samples were separated by filtration, dried and weighed. Subsequently these were sieved on a 200 mesh and the amounts of substance passing through the holes were weighed.

(d) *Swelling* : Percentage swelling measurements were made by allowing the samples to equilibrate in water overnight. The wet sample weight was taken as M_w and the corresponding dry weight M_d was obtained after drying the sample at 70°. The gravimetric percent (α) swelling was calculated as

$$\alpha = \frac{M_w - M_d}{M_d} \times 100.$$

(e) *Identification of inorganic groups* : The infrared spectra (KBr) of the samples were recorded on a Perkin-Elmer apparatus.

(f) *Exchange capacity* : Exchange capacity measurements were made by the method followed by Kunin[7]. The samples were converted into the H^+- form by washing with HCl followed by distilled water to remove acidity. Known weight of the samples in the H^+- forms were equilibrated with standard solution (0.01*M*) of Na, Ca^{II}, Mg^{II} and Zn^{II} ions.

$$\text{Resin-H}^+ + \text{M}^+ \rightleftharpoons \text{Resin-M}^+ + \text{H}^+$$

Test columns were prepared from graduated burettes with cotton-wool plugs and known weight of the sample. The sample was made into a slurry with distilled water. The burette column fitted with cotton-wool was filled with the slurry. Sodium sulphate solution (25 ml, 0.01*M*) was added slowly to the column in 2 or 3 portions. The eluted solution was collected. The H^+ liberated in the solution was titrated against standard NaOH solution (0.01*M*) with phenolphthalein as indicator.

The ion exchange resin was regenerated by washing it with HCl (25 ml, 4*M*) and subsequently with water. The filtrate was tested for the excess of chloride ion with silver nitrate. The resin was now filled with 25 ml portions of $Ca^{II}/Mg^{II}/Zn^{II}$ solutions of known strength at the rate of 2-3 ml min^{-1}. Solutions were prepared from calcium chloride, magnesium sulphate and zinc sulphate (all AnalaR) salts. The filtrate was collected and the amount of the ions exchanged were determined by titrating against standard EDTA. By this EDTA titration, the decrease in $Ca^{II}/Mg^{II}/Zn^{II}$ ion concentration in the supernatant was measured and the exchange capacity of the composites were calculated (Table 4)

Results and Discussion

The percentage composition and physical characteristics of the different exchangers are given in Table 1. The average swelling percentage and the densities are given in Table 2.

TABLE 2—PERCENTAGE SWELLING AND ABSOLUTE DENSITIES

Sample	Coconut charcoal in resin	Average swelling	Absolute density	
			In hydrated state	In dehydrated state
	%	%	g ml^{-1}	g ml^{-1}
A	0	122.90	2.298	1.599
B	20	89.45	1.472	1.643
C	25	92.60	1.352	1.627
D	30	90.36	1.393	1.580
E	40	97.68	1.318	1.612
F	60	112.80	1.401	1.490
G	80	120.30	1.395	1.499
H	100	128.80	1.374	1.482

The average percent swelling decreases from 100 percent resin to pure carbon. It is not necessary for a resin to swell in a solvent in order to exhibit appreciable ion exchange capacity. The results in column 3 of Table 2 show that the swelling of the pure resin is greater than other samples except pure

charcoal. From this it can be stated that the porosity and polarity are greater in the pure resin. But the swelling in the sample with 80 percent charcoal is higher than the samples with the less percentage of charcoal. This may be due to high porous nature of charcoal. Volumetric swelling is not high, because there are macroreticular and nongel pores.

The absolute densities both in the hydrated and dehydrated states are not much different between the pure resin and the composites. It shows high porous nature for the pure resin and the composites.

TABLE 3—ATTRITION EFFECT ON EXCHANGERS

Sample	Coconut charcoal in resin	Weight of resin taken before shaking	After shaking Amount passed through 200 mesh	
	%	g	g	%
A	0	1.8490	0.3684	19.93
B	20	1.6590	0.2416	14.56
C	25	1.6018	0.2324	14.5
D	30	1.5800	0.2142	13.80
E	40	1.5274	0.2970	19.45
F	60	1.7280	0.2648	15.32
G	80	1.9100	0.2552	13.35
H	100	1.9732	0.2460	12.45

As seen from column 3 of Table 3, the samples before shaking are basically made up of particles above 200 mesh in size. After shaking for several hours and repeating the sieving process it is observed that the percentage of particles less than 200 mesh in size formed due to attritional braking during sieving is not appreciable. This is the same for pure resin and the composites B to G. Thus, much difference is not seen in the attritional stability between the pure and the composites, although in the latter it is possible that the resin might have formed in the capillaries of charcoal particles.

The apparent capacity for the exchange of Na^+ (0.01*M*) and $Ca^{II}/Mg^{II}/Zn^{II}$ (0.01*M*) on the H^+-form of the exchangers are listed in Table 4.

TABLE 4—CAPACITY OF H^+-FORM OF COMPOSITES

Sample	Coconut charcoal in resin	Exchange column capacity estimated meq g^{-1}			
		Na 0.01*M*	Ca 0.01*M* EDTA	Mg 0.01*M* EDTA	Zn 0.01*M* EDTA
	%				
A	0	0.810	1.650	1.51	1.430
B	20	0.770	1.40	1.47	1.410
C	25	0.750	0.805	1.00	1.250
D	30	0.758	1.200	1.46	1.40
E	40	0.605	1.08	1.14	1.06
F	60	0.480	1.062	1.20	1.06
G	80	0.360	1.880	0.80	0.840
H	100	0.192	0.730	0.702	0.803

As expected the exchange capacities are higher for bivalent ions as compared to Na^+ at the same concentration. Fig. 1 shows the plot of column exchange capacity *vs* coconut fibre charcoal content in the resin for Na, Ca^{II}, Mg^{II}, and Zn^{II} ions. It is seen that though there is a continuous decrease in the capacity of coconut charcoal the fall is not much upto 30%. This indicates that substitution of coconut fibre charcoal upto 30% is economical.

The regidity of the matrix is proved from swelling measurements. So, these resins may be useful where they are required to stand large osmotic shock. The inherent porosity of these resins are proved by density measurements. Since they have inherent porosity the resins may be useful

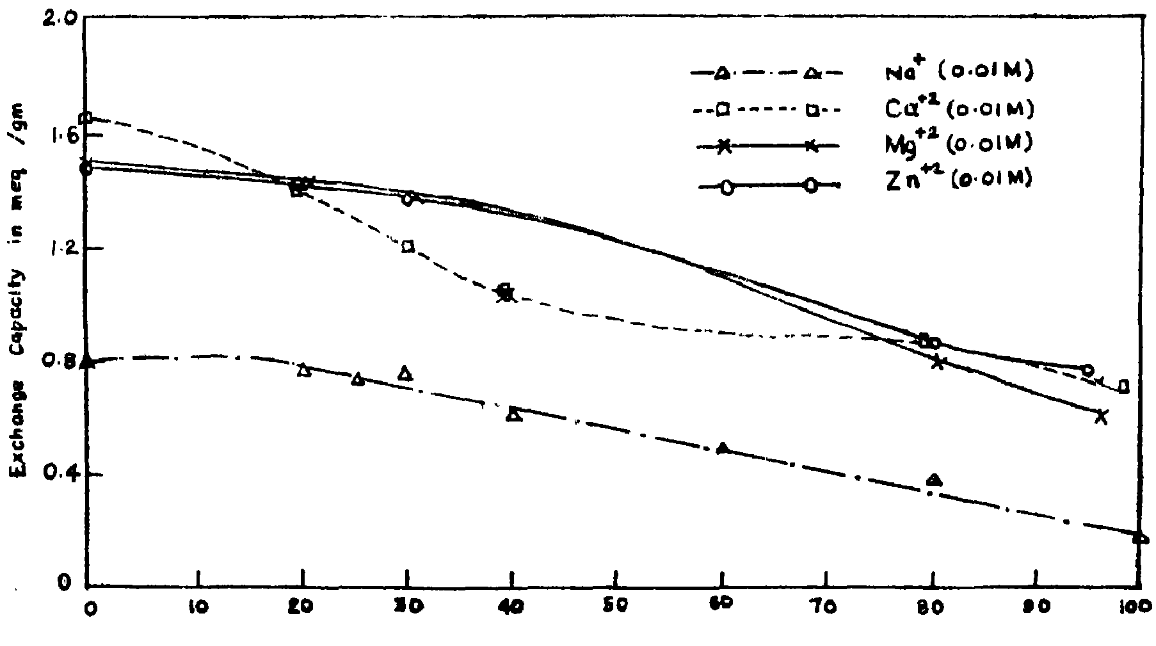


Fig. 1. Exchange capacity *vs* percentage of coconut fibre charcoal in the resin.

in nonaqueous solvents. As a result of porosity these resins may be used for the exchange of big ions of the type $(NR_4)^{4+}$ and hence, in pharmaceutical industry.

Acknowledgement

The authors are thankful to Prof. S. Nagarathinam, Principal, Regional Engineering College, Trichy and Dr. D. Venkappayya, Head, Department of Chemistry for providing facilities.

References

1. N. L. N. SARMA, M. JOSEPH and P. VASUDEVAN, *Res. Ind. (New Delhi)*, 1976, 21, 173.
2. P. VASUDEVAN and N. L. N. SARMA, *J. Appl. Polym. Sci.*, 1979, 24, 1443.
3. H. HEIMANH and R. RATNER, *Bull. Res. Council Isr.*, 1953, 3, 96.
4. G. J. M. RAO and S. C. PILLAI, *J. Indian Inst. Sci., Sect. A*, 1954, 36, 70.
5. N. V. OCTROOIEU and F. MAATSCHAPPIJ, Indian Pat. 828 222/1938.
6. D. K. HALE, *Chem. Ind.*, 1935, 1147.
7. R. KUNIN, "Ion-Exchange Resins", 3rd. ed., Wiley, New York, 1958.

Synthesis of Aryl Thioureas and Related Compounds as Potential Fungicides

V. K. MISHRA and S. C. BAHEL*

Chemistry Department, Gorakhpur University, Gorakhpur-273 001

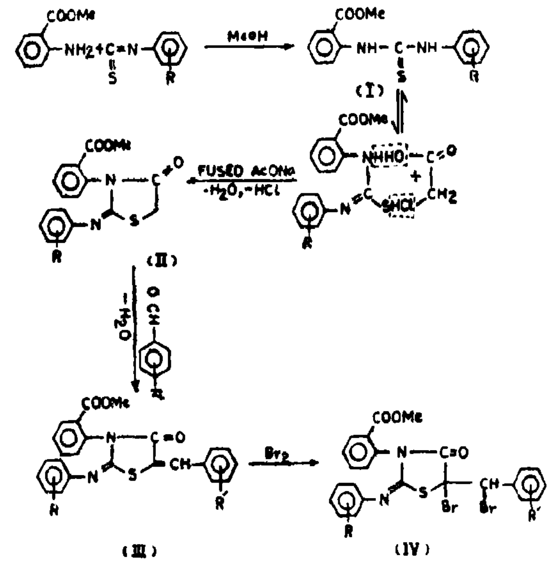
Manuscript received 10 June 1982, revised 16 July 1984, accepted 15 August 1984

THE pesticidal activity of substituted thioureas is due to the presence of N–C=S group. Various 4-thiazolidones are shown to possess pesticidal[1], miticidal[2], antimicrobial[3,4], antibacterial[5], antitubercular[6], amaebicidal[7], and fungicidal[8-10] activities. 3-Aryl-2-arylimino-4-thiazolidinones have also been reported for their fungicidal activity[11]. Keeping this in view some aryl thioureas, 4-thiazolidones and related compounds were prepared.

Methylanthranilate was condensed with aryl isothiocyanate to yield *N*-*o*-carbomethoxyphenyl-*N'*-aryl thioureas (I). I on heating with chloroacetic acid and fused sodium acetate gave the corresponding 3-*o*-carbomethoxyphenyl-2-aryliminothiazolid-4-ones (II), which with anhydrons sodium acetate and an aldehyde produced 5-arylideno-3-*o*-carbomethoxyphenyl-2-aryliminothiazolid-4-ones (III). III on bromination yielded the corresponding dibromides (IV).

Experimental

Melting points are uncorrected and purity of the compounds was checked by tlc. Structure assigned to II was confirmed by hydrolysis. The structure of the compounds was confirmed by elemental analysis, ir and nmr spectra. The ir spectra (KBr) were recorded on a Perkin-Elmer 190 spectrophotometer and nmr on Varian EM 360 spectrophotometer at 60 MHz.



R = –H, o–CH_3, p–CH_3.
R' = –H, –OH.

N-o-*Carbomethoxyphenyl*-N'-*arylthioureas* (1) : A methanolic solution of methyl anthranilate (0.01 *M*) and arylisothiocyanate (0.01 *M*) was refluxed for 3 h and cooled. The product separating out was filtered, washed and crystallised from aqueous ethanol. The compounds thus prepared are listed in Table 1.

3-o-Carbomethoxyphenyl-2-aryliminothiazolid-4-ones (II) : A methanolic solution of thiourea (I) (0.01 *M*), chloroacetic acid (0.01 *M*) and fused sodium acetate (2.0 g) was refluxed for 5 h, cooled and poured into water. The solid separating out was filtered, washed with water and crystallised with aqueous ethanol. The compounds thus prepared are given in Table 2.

Structural confirmation of II : A methanolic solution (10 ml) of the above 4-thiazolidone (1.0 g) and conc. HCl (2 ml) was refluxed for 3 to 4 h. Methanol was distilled off and the residue poured into water. The precipitate obtained was washed with water and crystallised. Each one of the compounds (II) was hydrolysed and the resulting compound 3-(*o*-carbomethoxyphenyl)thiazolidine-2,4-dione, had the same m.p. 240°. M.m.p. remained the same. It could not, however, be synthesised.

5-Arylideno-3-o-carbomethoxyphenyl-2-arylimino-thiazolid-4-ones (III) : A mixture of 3-*o*-carbomethoxyphenyl-2-aryliminothiazolid-4-one (0.01 *M*),

TABLE 1—*N*-*o*-CARBOMETHOXYPHENYL-*N'*-ARYLTHIOUREAS (I)*

Sl. no.	R	M.p. °C	Yield %	Molecular formula	Fungicidal activity, Concn. 10 ppm *A. flavus*	*H. oryzae*	*C. sacchari*
1.	H**	285	95.6	$C_{15}H_{14}N_2O_2S$	30.2	30.0	33.2
2.	*o*-CH_3	245	94.7	$C_{16}H_{16}N_2O_2S$	31.3	31.4	35.3
3.	*p*-CH_3	286	96.5	$C_{16}H_{16}N_2O_2S$	32.8	31.8	35.0

* Elemental analyses in good agreement with the calculated ones.
** ν_{max} 3200 (N—H stretch), 1730 (C=O aryl ester), 1080 cm^{-1} (C=S) and 760 (*ortho*-substituted benzene); δ (DMSO-d_6) 3.6 (s, 2H, NH), 4.1 (s, 3H, $COOCH_3$) and 7.4-8.0 (m, 9H, Ar).

TABLE 2—3-*o*-CARBOMETHOXYPHENYL-2-ARYLIMINOTHIAZOLID-4-ONES (II)*

Sl. no.	R	M.p. °C	Yield %	Molecular formula	Fungicidal activity, Concn. 10 ppm *A. flavus*	*H. oryzae*	*C. sacchari*
4.	H**	200	82.7	$C_{17}H_{14}N_2O_3S$	32.5	32.0	35.5
5.	*o*-CH_3	225	85.5	$C_{18}H_{16}N_2O_3S$	33.0	32.4	36.5
6.	*p*-CH_3	246	90.4	$C_{18}H_{16}N_2O_3S$	33.2	32.2	38.7

* Explanation as in Table 1.
** ν_{max} 1700 (C=O aryl ester), 1630 (CO—N tert-amine), 1600 (C=N) and 760 cm^{-1} (*ortho*-substituted benzene); δ(DMSO-d_6) 2.5 (s, 2H, CH_2), 3.32 (s, 3H, $COOCH_3$) and 7.3-8.0 (m, 9H, Ar).

TABLE 3—ARYLIDENO-3-*o*-CARBOMETHOXYPHENYL-2-ARYLIMINOTHIAZOLID-4-ONES (III)*

Sl. no.	R	R'	M.p. °C	Yield %	Molecular formula	Fungicidal activity Concn. 10 ppm *A. flavus*	*H. oryzae*	*C. sacchari*
7.	–H	–H**	291	75.4	$C_{24}H_{18}N_2O_3S$	–	–	–
8.	–H	–OH	295	77.6	$C_{24}H_{18}N_2O_4S$	40.6	40.3	42.5
9.	*o*-CH_3	–H	271	79.5	$C_{25}H_{20}N_2O_3S$	43.7	43.5	47.8
10.	*o*-CH_3	–OH	265	75 6	$C_{25}H_{20}N_2O_4S$	–	–	–
11.	*p*-CH_3	–H	276	80.2	$C_{25}H_{20}N_2O_3S$	–	–	–
12.	*p*-CH_3	–OH	220	82.3	$C_{25}H_{20}N_2O_4S$	44.6	44.7	48.3

* Explanation as in Table 1.
** ν_{max} 720 (C=O aryl ester), 1660 (CO—N tert-amide), 1620 (C=N), 760 (*ortho*-, *mono*-substituted benzene). and 690 cm^{-1} (-S-).

TABLE 4—5-ARYLIDENO-3-*o*-CARBOMETHOXYPHENYL-2-ARYLIMINOTHIAZOLID-4-ONE DIBROMIDES (IV)

Sl. no.	R	R'	M.p. °C	Yield %	Molecular formula	Fungicidal activity, Concn. 10 ppm *A. flavus*	*H. oryzae*	*C. sacchari*
13.	*o*-CH_3	OH	240	69.5	$C_{25}H_{20}Br_2N_2O_4S$	–	–	–
14.	*p*-CH_3	H**	210	72.3	$C_{25}H_{20}Br_2N_2O_3S$	47.5	47.0	50.3
15.	*p*-CH_3	OH	193	70.6	$C_{25}H_{20}Br_2N_2O_4S$	48.7	49.0	52.5
Memcge						75.4	78.2	72.8
Blitox 50 WP						73.5	79.5	78.3

* Explanation as in Table 1.
** ν_{max} 1730 (C=O aryl ester), 1650 (CO—N tert-amide), 1620 (C=N), 800 (*para*-substituted benzene), 760 (*ortho*-, *mono*-substituted benzene), 710 (—S—) and 680 cm^{-1} (C—Br).

arylaldehyde (0.01 *M*) and anhydrous sodium acetate (2.0 g) was refluxed in glacial acetic acid (10 ml) for 6 h and cooled. The resulting solution was poured into water and the solid separating was filtered, washed and crystallised from aqueous ethanol. The compounds thus prepared are given in Table 3.

5-Arylideno-3-o-carbomethoxyphenyl-2-arylimino-thiazol-4-one dibromides (IV): 5-Arylideno-3-*o*-carbomethoxyphenyl-2-aryliminothiazolid-4-one (0.005*M*) was dissolved in minimum amount of chloroform. To this, Br_2 (0.005 *M*) in chloroform was added dropwise with swirling. The solution was kept in an ice-bath for 4 h and shaken intermittently. On evaporation a solid residue was obtained which was washed with water and crystallised from aqueous ethanol. The compounds thus prepared are given in Table 4.

Fungicidal screening: The compounds were screened for their antifungal activity against *A. flavus*, *H. oryzae* and *C. sacchari* by agar-plate technique[18] at three different concentration, *viz*. 1000, 100 and 10 ppm. Two commercial fungicides Memcge and Blitox 50 WP have also been tested under similar conditions to compare the result. The number of replications in each case was three. The percentage inhibition of growth of fungus colony is given by the following expression.

$$\text{Percentage inhibition} = \frac{C-T}{C} \times 100$$

where C = diameter of fungus colony (mm) in control after 96 h,

T = diameter of fungus colony (mm) in presence of test chemical after 96 h.

Results and Discussion

Most of the compounds reported herein have been screened for their antifungal activity against *A. flavus*, *H. oryzae* and *C. sacchari* and found to possess moderate to fairly good level of fungicidal activity. However, they are slightly more toxic against *C. sacchari* than *A. flavus* and *M. oryzae*. In general, introduction of different groups and their position did not affect the toxicity to any marked degree. However, introduction of methyl group resulted in an increase of fungicidal activity. A comparison of compounds of Tables 1-4 shows that the dibromides (VI) are little more active than compounds III which inturn show slightly better activity than compounds II. The least active are the compounds I (Table 1). Compounds 14 and 15 are more active due to the presence of bromine.

Acknowledgement

The authors sincerely thank Prof. R. P. Rastogi, Head, Chemistry Department, Gorakhpur University, for providing facilities and Dr. R. H. Khan, East Carolina University for ir, nmr and elemental analyses. One of the authors (V. K. M.) is thankful to C. S. T., Lucknow for providing financial assistance.

References

1. K. C. Joshi and S. C. Bahel, *J. Indian Chem. Soc.*, 1962, 39, 121.
2. D'Silva and D. J. Themistodes, *U. S. Pat.* 3 966 953, 1976 (*Chem. Abstr.*, 1977, 86, 29794).
3. K. J. Mehta, A. C. Chawda and A. R. Parikh, *J. Indian Chem. Soc.*, 1979, 56, 173.
4. R. R. Shah, R. D. Mehta and A. R. Parikh, *J. Indian Chem. Soc.*, 1981, 58, 113.
5. K. J. Mehta and A. R. Parikh, *J. Inst. Chem., Calcutta*, 1978, 50, 67.
6. H. Tfniyama, S. Takemura, B. Yasni and H. Uchida, *J. Pharm. Soc. Jpn.*, 1954, 74, 113 (*Chem. Abstr.*, 1954, 48, 6504).
7. R. C. Gupta, R. Nath, K. Shanker, K. P. Bhargava and K. Kishore, *J. Indian Chem. Soc.*, 1978, 55, 832.
8. K. P. Jadhav and D. B. Ingle, *J. Indian Chem. Soc.*, 1978, 55, 424.
9. K. R. Manoj, P. C. Joshi, Jr. and P. C. Joshi, Sr., *J. Indian Chem. Soc.*, 1979, 56, 173.
10. K. P. Jadhav, M. S. Shingare and D. E. Ingle, *Acta Cience Indica*, 1978, 4, 141 (*Chem. Abstr.*, 1979, 90, 121473).
11. V. J. Ram and H. N. Pandey, *J. Indian Chem. Soc.*, 1972, 49, 181.
12. U. S. D. A. Circular No. 198, 1931.

Synthesis of Thiazolyl Compounds as Potential Fungicides

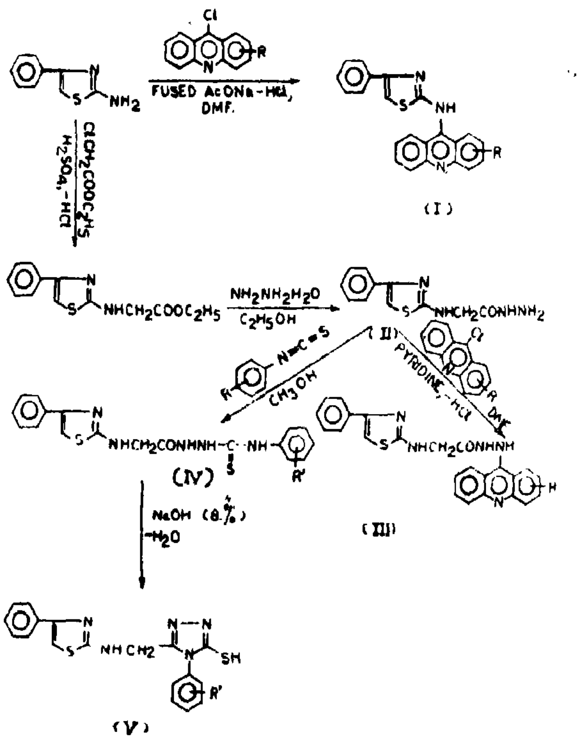
V. K. MISHRA and S. C. BAHEL*

Chemistry Department, Gorakhpur University, Gorakhpur-273 001

Manuscript received 10 June 1982, revised 16 July 1984, accepted 15 August 1984

THIAZOLES have been reported as insecticidal[1], antibacterial[2], antitubercular[3], antifungal[4], herbicidal[5], pesticidal[6] and local anaesthetic[7] agents. Acridines have been reported as insecticides[8] and fungicides[9], and compounds containing triazole ring have shown fungicidal[10], bactericidal[11] and pesticidal[12] activity. In view of these facts it was worth investigating the compounds having both the moieties.

2-Amino-4-phenylthiazole was condensed with 5-chloroacridine to yield 4-phenyl-2-(acridin-5-yl) aminothiazole (I). 4-Phenyl-(thiazol-2-yl)-aminoacetylhydrazine (VI) was reacted with 5-chloroacridine to yield *N*-(acridin-5-yl)-*N*[1]-(4″-phenylthiazole-2″-yl)-aminoacetylhydrazine (III). I on treatment with arylisothiocyanate yielded *N*-aryl-*N*′-(4″-phenylthiazol-2″-yl)aminoacetylthiosemicarbazide (IV) which on alkaline cyclisation yielded the corresponding triazole (V).



R = —H, 3-Cl, 1-CH$_3$, 3-CH$_3$,
R′ = H, *o*-CH$_3$, *p*-CH$_3$.

Experimental

Melting points are uncorrected and purity of the compounds was checked by tlc. Structure of

compounds were checked by elemental analyses, ir and nmr spectra. The ir spectra (KBr) were recorded on a Perkin-Elmer 197 spectrophotometer and nmr spectra on a Varian EM 360 spectrometer at 60 MHz.

4-Phenyl-2-(acridin-5-yl)-aminothiazoles (I) : A DMF (20 ml) solution of 2-amino-4-phenylthiazole (0.01 *M*), 5-chloroacridine (0.01 *M*) and fused sodium acetate (2 g) was refluxed for 6 h, cooled and poured into water. The solid obtained was filtered, washed and crystallised from aqueous ethanol. The results of compounds thus prepared are given in Table 1.

N-*(Acridin-5-yl)*-N'-*(4"-phenylthiazol-2"-yl)-aminoacetyl)hydrazine* (III) : A DMF (20 ml) solution of 5-chloroacridine (0.01 *M*), 4-phenyl-(thiazol-2-yl)-aminoacetylhydrazine (0.01 *M*) and pyridine (1 ml) was refluxed for 6 h, cooled and poured into water. The solid obtained was filtered, washed and crystallised from aqueous ethanol. The results of compounds thus prepared are given in Table 2.

N-*Aryl*-N'-*(4"-phenylthiazol-2"-yl)-aminoacetylthiosemicarbazide* (IV) : A methanolic solution of 4-phenylthiazol-2-yl-aminoacetylhydrazine (0.01 *M*) and arylisothiocyanate (0.01 *M*) was refluxed for 6 h and cooled. The solid obtained was filtered, washed and crystallised from aqueous ethanol. The results of compounds thus prepared are listed in Table 3.

3-(4'-Phenylthiazoyl-2'-yl)-aminoacetyl-4-aryl-5-mercapto-1, 2, 4-triazoles (V) : *N*-Aryl-*N'*-(4"-phenylthiazol-2-yl)-aminoacetylthiosemicarbazide (0.01*M*) was refluxed with NaOH solution (25 ml, 8%) for 5 h and poured into water and filtered. The filtrate on acidification gave a solid, which was filtered, washed and crystallised from aqueous ethanol. The results of compounds thus prepared are listed in Table 4.

TABLE 1—4-PHENYL-2-(ACRIDIN-5'-YL)-AMINOTHIAZOLES (I)*

Sl. no.	R	M.P. °C	Yield %	Molecular formula	Fungicidal activity, Concn. 10 ppm A. flavus	H. oryzae	C. sacchari
1.	H[a]	200d	95.6	$C_{22}H_{15}N_3S$	29.7	29.5	30.6
2.	3-Cl[b]	210d	86.5	$C_{22}H_{14}ClN_3S$	35.0	35.6	40.7
3.	1-CH_3	225d	92.3	$C_{23}H_{17}N_3S$	–	–	–
4.	3-CH_3	185d	94.0	$C_{23}H_{17}N_3S$	–	–	–

* Elemental analyses in good agreement with the calculated ones.
[a] δ(DMSO-d_6+$CDCl_3$) 4.2 (s, 1H, vinyl), 6.8 (s, 1H, NH) and 7.2-7.8 (m, 13H, Ar).
[b] ν_{max} 3430 (NH secondary), 1580 (C=N conjugated cyclic), 750 (monosubst. benzene), 710 (—S—) and 620 cm^{-1} (C—Cl).

TABLE 2—*N*-(ACRIDIN-5-YL)-*N'*-(4"-PHENYLTHIAZOL-2"-YL)-AMINOACETYLHYDRAZINES (III)

Sl. no.	R	M.p. °C	Yield %	Molecular formula	Fungicidal activity, Concn. 10 ppm A. flavus	H. oryzae	C. sacchari
5.	—H	200[d]	85.2	$C_{24}H_{19}N_5OS$	32.2	32.7	33.3
6.	3-Cl	283	86.0	$C_{24}H_{18}ClN_5OS$	–	–	–
7.	1-CH_3**	320	80.7	$C_{25}H_{21}N_5OS$	–	–	–
8.	3-CH_3	180[d]	84.5	$C_{25}H_{21}N_5OS$	40.4	40.5	43.7

* Explanation as in Table 1.
** ν_{max} 3440 (NH secondary), 1690 (CONH secondary), 1620 (C=N conjugated cyclic), 1385 (C–CH_3), 750 (monosubst. benzene) and 710 cm^{-1} (–S–) ; δ(DMSO-d_6+$CDCl_3$) 2.7 (s, 3H, CH_3), 3.4(S, 2H, NCH_2CO), 6.82 (m, 3H, NHNHCOCHNH) and 7.2-74 (m, 12H, Ar).

TABLE 3—*N*-ARYL-*N'*-(4"-PHENYLTHIAZOL-2"-YL)-AMINOACETYLTHIOSEMICARBAZIDES (IV)*

Sl. no.	R	M.p °C	Yield %	Molecular formula	Fungicidal activity, Concn. 10 ppm A. flavus	H. oryzae	C. sacchari
9.	H	225	79.2	$C_{18}H_{17}N_5OS_2$	–	–	–
10.	*o*-CH_3**	134	75.6	$C_{19}H_{19}N_5OS_2$	43.2	43.4	45.0
11.	*p*-CH_3	66	80.6	$C_{19}H_{19}N_5SO_2$	43.2	43.8	45.5

* Explanation as in Table 1.
** ν_{max} 3425 (NH secondary), 1700 (CONH secondary), 1600 (C=N conjugated cyclic), 1080 (C=S) and 770 cm^{-1} (mono/*o*-subst. benzene).

TABLE 4—ARYL-*N*-(4"-PHENYLTHIAZOL-2'-YL)-AMINOMETHYL-4-ARYL-5-MERCAPTO-1,2,4-TRIAZOLES (V)*

Sl. no.	R	M.p. °C	Molecular formula	Fungicidal activity, Concn. 10 ppm A. flavus	H. oryzae	C. sacchari
12.	—H**	68.5	$C_{18}H_{15}N_5S_2$	44.2	44.0	50.5
13.	*o*-CH_3	76.0	$C_{19}H_{17}N_5S_2$	–	–	–
14.	*p*-CH_3	75.6	$C_{19}H_{17}N_5S_2$	45.7	45.8	53.6
				75.5	78.3	72.8
Memcge				73.5	79.5	78.3
Blitox 50 WP						

* Explanation as in Table 1.
** ν_{max} 3400 (NH secondary), 2600 (SH), 1690 (C=N conjugated cyclic) and 760 cm^{-1} (monosubst. benzene) ; δ(DMSO-d_6+$CDCl_3$) 3.3 (s, 2H, CH_2), 6.6 (s, 1H, NH), 4.2 (s, 1H, vinyl) and 7.6-78 (m, 10H, Ar).

Fungicidal screening : The compounds were screened for antifungal activity against *A. flavus*, *H. oryzae* and *C. sacchari* by agar plate technique[13] at three different concentrations, *viz*. 1000, 100 and 10 ppm. Two commercial fungicides Memcge and Blitox 50 WP were also tested under similar conditions to compare the result. The number of replication in each case was three. The percentage inhibition of growth of fungus colony is given by the following expression.

$$\text{Percentage inhibition} = \frac{C-T}{C} \times 100$$

where C = diameter of fungus colony (mm) in control after 96 h,

T = diameter of fungus colony (mm) in presenceof test chemical after 96 h.

Results and Discussion

Most of the compounds screened possess moderate to fairly good level of fungicidal activity against all the three fungi showing more activity against *C. sacchari*. Introduction of different groups and their position did not affect the toxicity to any marked degree. However, compounds containing CH_3 group were found to be more active than the unsubstituted compounds.

A comparison of thiazolyl compounds (Tables 1-4) shows the following order of antifungal activity.

compounds IV > compounds III > compounds II > compounds I. Highly active compounds of the series contain a thiazolyl and a triazolyl moiety.

Acknowledgement

The authors sincerely thank Prof. R. P. Rastogi, Head, Chemistry Department, Gorakhpur University for providing facilities and, Dr. R. H. Khan, East Carolina University, U.S.A. for ir and elemental analysis. One of the authors (V.K.M.) is thankful to C.S.T., Lucknow for providing financial assistance.

References

1. G. BECKAND and D. ARTT, *Ger. Pat.* 2451632/1976.
2. J. SHUKRI, A. SHUBBER, F. ALCHALABI, K. A. KHALIFA and K. F. HASSAN, *Iraqi. J. Sci.*, 1979, **20**, 75(*Chem. Abstr.*, 1979, **91**, 140762).
3. D. B. INGLE, M. S. SHINGARE and V. H. PATIL, *J. Indian Chem. Soc.*, 1978, **55**, 50.
4. K. C. JOSHI, S. GIRI and S. C. BAHEL, *J. Sci. Ind. Res.*, *Sect. C*, 1962, **21**, 315.
5. G. BOROSCHEWSKI and F. ARNDI, *Ger. Pat.* 2264983/1975.
6. J. P. NATH, M. DASH, D. N. ROUT and G. N. MAHAPATRA, *Indian J. Chem.*, *Sect. B*, 1979, **18**, 384.
7. P. N. BHARGAVA, S. PRAKASH and D. H. SINGH, *J. Indian Chem. Soc.*, 1978, **55**, 726.
8. W. D. STEWART and J. H. HANDEN, *U. S. Pat.* 2510431/1950 (*Chem. Abstr.*, 1950, **44**, 8591).
9. R. H. KHAN and S. C. BAHEL, *J. Indian Chem. Soc.*, 1976, **53**, 837.
10. G. MEUBACHO, B. SACHSE and H. BUELSTILL, *Ger. Pat.* 2826760/1980 (*Chem. Abstr.*, 1980, **92**, 181200).
11. S. C. BENNUR, V. C. JIGAJINNI and V. V. BADIGER, *Rev. Roum. Chim.*, 1976, **21**, 757 (*Chem. Abstr.*, 1976, **85**, 943006).
12. M. A. WEDD and J. H. PARSONS, *Ger. Pat.* 2653447/1977 (*Chem. Abstr.*, 1977, **86**, 117870).
13. U S. D. A., Circular No. 198, 1931.

Alkaloid Contents of *Lupinus hartwegii* Roots

R. RASTOGI*

Department of Chemistry, University of Rajasthan, Jaipur-302 004

and

T. R. RAJAGOPALAN

Department of Chemistry, University of Delhi, Delhi-110 007

Manuscript received 12 November 1982, accepted 9 March 1984

LUPINUS hartwegii (Leguminosae), an annual herb, is a highly crossbred cultivar grown in gardens as winter ornamental[1,2]. The plant has been investigated earlier by different workers for quinolizidine alkaloids[2-4]. No work has been reported so far on the roots of this species.

The present work deals with the isolation and characterisation of three quinolizidine and one indole alkaloid from the $CHCl_3$ extract of *L. hartwegii* roots.

Completely air dried and coarsely ground roots (500 g) were exhaustively extracted in a soxhlet extractor successively with petroleum ether (60-80°) and ethanol (95%). The ethanol extract was worked up with $CHCl_3$ by the usual procedure for the isolation of alkaloids[5]. The $CHCl_3$ extract, on column chromatography over neutral Al_2O_3 gave four alkaloids (compounds A-D), which were visualised on tlc plates by spraying iodoplatinate reagent[6].

Compound A (aphylline) was crystallised from petroleum ether as colourless needles (30 mg), m.p. 99-101° (Lit[7]. m.p. 100-101°); perchlorate, m.p. 233°; ν_{max} (KBr)[8] 2970, 1640, 1455 and 1280 cm^{-1}; *m/e*[9] 248 (M^+), 247, 220, 137, 136, 98, 97, 96 and 84.

Compound B (lupanine) was crystallised from petroleum ether as colourless flakes (175 mg), m.p. 97-98°; perchlorate, m.p. 224°; co-tlc, m.m.p. and superimposable ir with an authentic sample confirmed the identity[9,10].

Compound C (nuttaline) was crystallised from acetone as colourless needles (35 mg), m.p. 107-109° (Lit.[11] m.p. 108-109°); perchlorate, m.p. 170-172°; ν_{max} (KBr)[11] 3480, 2810, 2760, 1650 and 1012 cm^{-1}; *m/e*[12] 264 (M^+), 246, 236, 154, 153, 152, 123, 84 and 55.

* Regional Chemical Laboratory, O.N.G.C., Baroda-390 009.

Compound D (gramine) was crystallised from acetone as colourless needles (60 mg), m.p. 134°; perchlorate, m.p. 150-151°; identified[13] by direct comparison with an authentic sample.

Acknowledgement

Thanks are due to Prof. R. O. Martin, Department of Biochemistry, University of Saskatchewan, Canada for supplying authentic lupanine and gramine, and to Dr. (Miss) K. Zutshi, Department of Chemistry, University of Rajasthan for helpful suggestions.

References

1. C. R. BABU, "Herbaceous Flora of Dehradun", C.S.I.R., New Delhi, 1977.
2. J. N. ANDERSON and R. C. MARTIN, *J. Org. Chem.*, 1976, **41**, 3441.
3. N. A. MAI'SURYAN and M. M. EDEL'SHTEIN, *Vestn. Sel. Nauk.*, 1960, **5**, 64.
4. E. P. WHITE, *New Zealand J. Sci. Technol., Part B*, 1957, **38**, 718.
5. R. RASTOGI and T. R. RAJAGOPALAN, *Pharmazie*, 1982, **37**, 75.
6. R. MUMER and M. MACHEBOUEF, *Bull Soc. Chim. Biol.*, 1949, **31**, 144.
7. Y. TSUDA and L. MARION, *Can. J. Chem.*, 1964, **42**, 764.
8. J. SKOLIK, M. WIEWIOROWSKI and K. JEDRZEJCZAK, *Bull. Acad. Pol. Sci., Ser Sci. Chim.*, 1969, **17**, 201.
9. J. N. ANDERSON and R. O. MARTIN, "Registry of Mass Spectra Data", Wiley, New York, 1973.
10. L. MARION, D. A. RAMSAY and R. N. JONES, *J. Am. Chem. Soc.*, 1951, **73**, 305.
11. S. T. GOLDBERG and V. M. BALTHIS, *J. Chem. Soc. D*, 1969, 660.
12. Y. D. CHO and R. O. MARTIN, *Anal. Biochem.*, 1971, **44**, 40.
13. I. RIBAS-MARQUES and M. REGUEIRO-GARCIA, *An. Quim.*, 1971, **67**, 93.

An Efficient Method for Estimation of Trace Level Mercury in Chlor-alkali Effluents

U. MURALIKRISHNA*, V. M. RAO
and
M. V. S. SURYANARAYANA

Department of Chemistry, Andhra University, Waltair-530 003

Manuscript received 13 March 1984, accepted 20 September 1984

THE high toxicity of mercury and its presence in many unsuspected sources have prompted many workers to recommend methods to eliminate the sources of its contamination or to reduce its content maximally. In recent years there has been considerable interest for developing better methods for the removal of mercury from aqueous solutions. Every method suffers from one or the other drawback. We now report an efficient method of removal of chloride, followed by the separation and determination of mercury at trace level by extraction with ethylacetate. The suitability of the method for the removal of mercury from effluent samples of chlor-alkali industry has been verified.

*Department of Chemistry, Andhra University P. G. Extension Centre, Nuzvid-521 201.

Experimental

Materials: A stock solution (mg ml^{-1}) of mercuric chloride was prepared and diluted appropriately. The tracer ^{203}Hg in the form of solution of mercuric nitrate in nitric acid was supplied by B.A.R.C., Bombay. Ethylacetate was used after purification by distillation. All other chemicals used were sufficiently pure.

Effluent samples from a chlor-alkali industry situated in Andhra Pradesh, were collected from different spots. Care was taken not to introduce excessive air into the samples.

Equipment: An E.C.I.L. S.C. 604 single channel analyser coupled with a 3" well type scintillation detector and an E.C.I.L. M.A. 5800A mercury analyser were used.

Procedure for extraction of mercury: 15 ml of the aqueous phase containing 45000 counts for 50 ml^{-1} of mercury tracer and appropriate concentrations of mercury at 35° was extracted briskly for 5 min with an equal volume of ethylacetate in a 60 ml separatory funnel. After allowing for 10 min the layers were separated and analysed using scintillation counter.

Procedure for the estimation of mercury in effluents: The pH of the effluent was adjusted to 2–3 and the chloride content in the sample was initially determined by potentiometric titration using silver nitrate. Stoichiometric amounts of the solution of lead acetate (20%) containing glacial acetic acid (1%) and sodium fluoride (1%) solutions were added to the effluent and stirred well. The resultant precipitate (PbClF) was allowed to digest on a water bath for 1 h. The precipitate was filtered through a sintered glass crucible, washed several times with saturated lead acetate solution and water. The filtrate was transferred into a 250 ml volumetric flask and made up to the mark with water. Mercury was extracted with ethylacetate[1] and its content assayed.

Results and Discussion

The mechanism of the extraction of mercury from aqueous solutions with ethylacetate is through the formation of a solvated species of the type $HgCl_2.2S$ (S=ethylacetate[1,2]). Using the standard procedure for the extraction[1], the pertinent variables such as pH, chloride concentration and extractant, were studied and the optimum conditions for the extraction were determined.

The results on the study of interferences show that the tolerence of diverse ions is fairly good. Since chloride is a serious interference in the

TABLE 1—ADSORPTION OF MERCURY ON PbClF

Total vol. of solution = 10 ml

Chloride mg ml^{-1}	Mercury µg ml^{-1}	% Adsorption on 1 g of PbClF
5.55	1.00	3.80
7.40	1.00	7.00
11.10	1.00	12.50
14.80	1.00	15.00
22.20	1.00	15.10
7.40	5.00	6.00
7.40	12.50	2.10
7.40	15.00	1.00
7.40	20.00	0.45
7.40	25.00	0.38

and attained a minimum value of 0.5, which is negligible. This clearly shows that in the precipitation of chloride as PbClF in the presence of mercury (20 µg ml^{-1}) from chloride solutions (7.5 mg ml^{-1}), the loss of mercury due to adsorption is negligible. Therefore, in order to avoid interference of chloride in the extraction of mercury by ethylacetate, precipitation of chloride as PbClF was carried out prior to the extraction step. The results of the analysis of the samples, synthetic and those obtained from the chlor alkali industry, are presented in Table 2.

TABLE 2—ANALYSIS OF SAMPLES

Sample	[Hg^{2+}] taken µg ml^{-1}	Directed method [Hg^{2+}] found Mercury analyser	Extraction method [Hg^{2+}] recovered Mercury analyser	Extraction method [Hg^{2+}] recovered Substoichiometric
Synthetic	5.0	5.0±0.006	4.987±0.026	4.962±0.026
Synthetic	10.0	9.991±0.024	9.980±0.004	9.998±0.011
Synthetic	20.0	19.995±0.015	19.968±0.002	20.017±0.009
Synthetic	25.0	23.013±0.004	25.047±0.005	25.020±0.008
Effluent	—			
Sample 1 (at point of emission)	—	18.802±0.007	18.750±0.024	18.847±0.021
Sample 2 (at 2 m down stream)	—	15.447±0.021	15.501±0.016	15.497±0.005
Sample 3 (at 10 m down stream)	—	1.500±0.001	1.479±0.003	1.600±0.012

extraction of mercury, removal of chloride from sample solutions prior to extraction is necessary. Removal of chloride in presence of mercury by precipitation as silver chloride resulted in the loss of 20-25% of mercury, due to the adsorption of mercury on the precipitate. Further, the precipitate is not easily filterable even after digestion for a long time. On the other hand, the adsorption of mercury on lead chlorofluoride under suitable conditions is negligible. Hence, the precipitation of PbClF, a procedure[3,4] usually chemists use to estimate fluoride content in rocks, has been made use of in the removal of chloride prior to the extraction step. Experiments were conducted using ^{203}Hg tracer to study the adsorption of mercury at trace level on the precipitate, PbClF, as a function of chloride and mercury concentrations in the solutions (Table 1). From the results it can be seen that with the variation of chloride in solution, the percent-adsorption of mercury on PbClF increased upto a limiting value, 15. On the other hand, the variation of mercury concentration at a fixed chloride concentration in solution, the percent-adsorption decreased gradually with the increase of mercury concentration

The proposed method is selective for the separation of trace amounts of mercury from chloride solutions (0.1*M*). The advantage of the proposed method lies in the use of ethylacetate as extractant for the separation of mercury. Ethylacetate is a readily available solvent at a low cost compared to other high molecular weight amines[5,6].

Acknowledgement

Thanks are due to U.G.C., New Delhi for financial assistance.

References

1. U. MURALIKRISHNA, V. M. RAO and M. V. S. SURYANARAYANA, *Z. Anal. Chem.*, 1982, **310**, 429.
2. U. MURALIKRISHNA, V. M. RAO and M. V. S. SURYANARAYANA, *Indian J. Chem., Sect. A*, 1983, **22**, 179.
3. G. STARCK, *Z. Anorg. Chem.*, 1911, **70**, 173.
4. F. G. HAWLEY, *Ind. Eng. Chem., Anal. Ed.*, 1926, **18**, 573.
5. F. L. MOORE, *Environ. Sci. Technol.*, 1972, **6**, 525.
6. F. L. MOORE, *Environ. Lett.*, 1975, **10**, 77.

J. Indian Chem. Soc.,
Vol. LXI, October 1984, pp. 921

ERRATA

Vol. LXI, May 1984 :

Page 450, lines 30-31, read,

J. Chem. Soc., 1953, 3397 ; 1954, 2904.

Vol. LXI, July 1984 :

Cover page 3, lines 55-56 read,

Officer-on-Special Duty

S. K. Roy, Ph.D., D.I.C.

Cover page 4, read,

Dr. S. K. Roy, for Shri Prabir K. Gupta.

Page 611, below line 9, read,

Manuscript received 26 September 1983, revised 2 April 1984, accepted 30 May 1984

J. Indian Chem. Soc.,
Vol. LXI, October 1984.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 923-925

Synthesis and Physico-chemical Studies of Some Binuclear Mixed Carboxylates of Copper(II)

B. P. BARANWAL†, G. K. PARASHAR‡ and R. C. MEHROTRA*

Chemical Laboratories, University of Rajasthan, Jaipur-302 004

Anhydrous copper(II) acetate undergoes substitution reactions with higher carboxylic acids refluxing in toluene, yielding soluble copper(II) carboxylates with general formula $Cu(OOCCH_3)_{2-n}(OOCR)_n$ (where $R = C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$ and $C_{21}H_{43}$ and n=1 or 2). These complexes on recrystallisation from benzene-alcohol mixtures form alcoholate complexes with the formulae, $Cu(OOCCH_3)(OOCR).R'OH$ and $Cu(OOCR)_2.R'OH$ (where R' = Me, Et and Pr^i). Elemental analyses, infrared and electronic spectra, magnetic measurements and ebullioscopic molecular weight determination of all the above complexes indicate their dimeric nature with carboxylate groups acting as bridging ligands.

THE chemistry of copper(II) carboxylates has been one of the most widely investigated topics in the field of metal carboxylates in view of their interesting magnetic and structural properties arising from possible superexchange metal-metal interactions[1-3]. A survey of the literature revealed[4] that while an extensive amount of work has been carried out on the addition complexes of copper(II) carboxylates, almost no work has been done on their substitution reactions. It was, therefore, considered of interest to investigate the substitution reactions of copper(II) acetate with higher carboxylic acids. It has been found that these reactions are quite facile and yield mixed carboxylates, $Cu(OOCCH_3)(OOCR)$ as well as anhydrous dicarboxylates, $Cu(OOCR)_2$, and both crystallise out with an adduct alcohol molecule from benzene-alcohol mixtures. Various physico-chemical studies have been carried out to throw light on the structure of all these derivatives.

Experimental

All the reactions were carried out under anhydrous conditions and glass apparatus with standard joints was used. The carboxylic acids were purified by distillation. Toluene was dried over sodium. Copper acetate was made anhydrous by refluxing its hydrated form with acetic anhydride followed by drying *in vacuo*.

Physico-chemical studies were made as described earlier[5]. Copper was estimated iodometrically with sodium thiosulphate and acetic acid, with standard sodium hydroxide solution using phenolphthalein as indicator. Alcohols were estimated by the oxidimetric method[6].

Reactions of copper acetate with higher carboxylic acids : To weighed amounts of copper acetate suspended in toluene were added carboxylic acids in the required proportions and the reaction mixtures were refluxed for 4-6 h. As the liberated acetic acid was removed azeotropically (106°) with toluene, the products dissolved in the solvent. The products were then recrystallised from benzene-alcohol (R'OH) mixture (4 : 1) and finally, the alcoholate complexes of mixed as well as dicarboxylate derivatives were obtained after removing the volatile solvents from the crystalline mass under vacuum at room temperature. The products on heating under vacuum (120°/1 mm) lost the alcohol of addition, yielding coloured crystalline solids. Detailed experimental results are summarised in Tables 1 and 2.

Results and Discussion

Substitution reactions of anhydrous copper(II) acetate have been carried out with higher carboxylic (myristic, palmitic, stearic and behenic) acids in different stoichiometric ratios refluxing in toluene.

$$Cu(OOCCH_3)_2 + n\ RCOOH \xrightarrow{\text{Toluene}} Cu(OOCCH_3)_{2-n}(OOCR)_n + n\ CH_3COOH$$

where $R = C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$ and $C_{21}H_{43}$, and n = 1 or 2.

These reactions may also be considered as transacylation reactions. The use of toluene as a solvent makes it easier to remove acetic acid liberated during the course of reactions azeotropically and made it possible to carry out the above reactions in 1 : 1 as well as in 1 : 2 molar ratios. The reactions are found to be facile and their progress was followed by estimating the liberated acetic acid content of the azeotrope collected during

† University of Gorakhpur, Gorakhpur.
‡ Shradhanand College, Delhi University, Delhi.

TABLE 1—REACTION PRODUCTS OF COPPER(II) ACETATE AND CARBOXYLIC ACIDS

Sl. no.	Reactants g	Molar ratio	Product and state	Acetic acid in azeotrope (g) Found/(Calcd.)	Copper (%) Found/ (Calcd.)	Mol. Wt.* Found/ (Calcd.)	μ_{eff} B.M.	$^{2}A_{1g} \rightarrow {}^{2}B_{1g}$ cm^{-1}
1.	$Cu(OOCCH_3)_2 + C_{13}H_{27}COOH$ 1.0 1.2	1 : 1	$Cu(OOCCH_3)(OOCC_{13}H_{27})$ green solid	0.32 (0.33)	18.05 (18.16)	723 (350)	1.42	15880
2.	$Cu(OOCCH_3)_2 + C_{13}H_{27}COOH$ 0.9 2.3	1 : 2	$Cu(OOCC_{13}H_{27})_2$ green solid	0.60 (0.61)	12.19 (12.26)	1018 (518)	1.43	15827
3.	$Cu(OOCCH_3)_2 + C_{15}H_{31}COOH$ 2.9 4.1	1 : 1	$Cu(OOCCH_3)(OOCC_{15}H_{31})$ green solid	0.96 (0.98)	16.73 (16.81)	729 (378)	1.43	15840
4.	$Cu(OOCCH_3)_2 + C_{15}H_{31}COOH$ 1.6 4.5	1 : 2	$Cu(OOCC_{15}H_{31})_2$	0.98 (1.06)	10.95 (11.06)	1108 (574)	1.46	15810
5.	$Cu(OOCCH_3)_2 + C_{17}H_{35}COOH$ 2.1 3.3	1 : 1	$Cu(OOCCH_3)(OOCC_{17}H_{35})$ greenish blue solid	0.68 (0.70)	15.56 (15.65)	791 (406)	1.38	15827
6.	$Cu(OOCCH_3)_2 + C_{17}H_{35}COOH$ 1.4 4.4	1 : 2	$Cu(OOCC_{17}H_{35})_2$ green solid	0.90 (0.93)	10.02 (10.08)	1162 (630)	1.37	15285
7.	$Cu(OOCCH_3)_2 + C_{21}H_{43}COOH$ 0.5 0.9	1 : 1	$Cu(OOCCH_3)(OOCC_{21}H_{43})$ greenish blue solid	0.16 (0.17)	13.53 (13.75)	901 (462)	1.40	15340
8.	$Cu(OOCCH_3)_2 + C_{21}H_{43}COOH$ 0.7 2.6	1 : 2	$Cu(OOCC_{21}H_{43})_2$ green solid	0.41 (0.46)	8.51 (8.55)	1458 (748)	1.42	15120

* In chloroform.

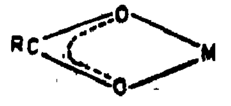
TABLE 2—ALCOHOLATE ADDUCTS OF CARBOXYLATE COMPLEXES OF COPPER(II)

Sl. no.	Compound	Solvent*	Product and state	Analysis (%): Found/(Calcd.) Copper	Alcohol	Mol. Wt* Found/ (Calcd.)	μ_{eff} B.M.	$^{2}A_{1g} \rightarrow {}^{2}B_{1g}$ cm^{-1}
1.	$Cu(OOCCH_3)(OOCC_{13}H_{27})$	MeOH	$Cu(OOCCH_3)(OOCC_{13}H_{27}).MeOH$ light green solid	16.46 (16.68)	—	780 (382)	1.43	15400
2.	$Cu(OOCC_{13}H_{27})_2$	MeOH	$Cu(OOCC_{13}H_{27})_2.MeOH$ light green solid	11.44 (11.54)	—	1142 (550)	1.45	15810
3.	$Cu(OOCCH_3)(OOCC_{15}H_{31})$	EtOH	$Cu(OOCCH_3)(OOCC_{15}H_{31}).EtOH$ light green solid	14.91 (14.98)	10.77 (10.86)	861 (424)	1.46	15285
4.	$Cu(OOCC_{15}H_{31})_2$	$Pr^{i}OH$	$Cu(OOCC_{15}H_{31})_2.Pr^{i}OH$ greenish blue solid	10.21 (10.02)	9.33 (9.48)	1202 (634)	1.49	15220
5.	$Cu(OOCCH_3)(OOCC_{17}H_{35})$	$Pr^{i}OH$	$Cu(OOCCH_3)(OOCC_{17}H_{35}).Pr^{i}OH$ greenish blue solid	13.54 (13.63)	12.81 (12.89)	—	1.40	15170
6.	$Cu(OOCC_{17}H_{35})_2$	EtOH	$Cu(OOCC_{17}H_{35})_2.EtOH$ light green solid	9.46 (9.39)	6.72 (6.81)	—	1.40	15100
7.	$Cu(OOCCH_3)(OOCC_{21}H_{43})$	MeOH	$Cu(OOCCH_3)(OOCC_{21}H_{43}).MeOH$ bluish green solid	12.77 (12.86)	—	—	1.42	15260
8.	$Cu(OOCC_{21}H_{43})_2$	MeOH	$Cu(OOCC_{21}H_{43})_2.MeOH$ light green solid	8.41 (8.90)	—	—	1.45	15080

* Plus benzene.

continuous fractionation. Mono- and di-substituted products have been obtained in quantitative yields.

All the derivatives are coloured, non-volatile solids and are soluble in benzene and toluene, but they are insoluble in alcohols ; these are, therefore, precipitated by adding alcohol to a benzene solution. On heating again the precipitated products dissolved and on cooling, coloured crystals were obtained with the formula $Cu(OOCCH_3)_{2-n}(OOCR)_n.R'OH$ (R' = Me, Et and Pr^i, and n = 1 or 2). The adduct-molecule of alcohol appears to be lost at ~120°/1 mm pressure leaving the mixed as well as dicarboxylate derivatives of copper without any adduct-alcohol molecule. It may be emphasised that transacylation method appears to be particularly suited for the synthesis of mixed carboxylate derivatives of copper(II) which can not be so easily synthesised by any other route. The solubility of mixed soap derivatives, $Cu(OOCCH_3)(OOCR)$, shows that these products are not equimolar mixtures of $Cu(OOCCH_3)_2$ and $Cu(OOCR)_2$ as the former is insoluble in benzene or toluene.

Infrared spectra : Infrared spectra (KBr) of all the complexes were recorded in the range 400-4000 cm^{-1}. In these spectra, the characteristic ~1710 (C=O stretching), ~3300 (OH stretching) and ~935 cm^{-1} (OH deformation) vibrations of free carboxylic acids[7] were found completely missing from their respective regions. The spectra, however, exhibited strong bands at ~1590 and ~1460 cm^{-1} which may be assigned to antisymmetric and symmetric C–O stretching vibrations (ν_a and ν_s)[8] ; the observed shifts towards higher side in these bands from 1578 and 1414 cm^{-1}, respectively in the spectrum of acetate ion[9] may be attributed to coordinated state of the carboxylate moiety. Out of the two possible modes[10] of coordination  and



, the latter appears to be more probable on the basis of the higher value of ν_s ; this is corroborated by the appearance of ν_s at the same position (1590 cm^{-1}) in the spectrum of $[Cu(OOCCH_3)_2 . H_2O]_2$ in which bridging type of coordination has been established by *X*-ray studies. In alcoholate complexes, the OH stretching vibration is found to be present at ~3000 cm^{-1} and the lowering in its value indicates the coordinating nature of the alcohol molecules[8]. Some other vibrations below 700 cm^{-1} may be ascribed to Cu – O stretching vibrations.

Electronic spectra and magnetic moments : Electronic spectra (nujol/benzene) of all the carboxylate derivatives have been recorded in the range 12500-25000 cm^{-1} and no marked difference could be observed in their spectra. The spectra exhibit a very broad antisymmetric band around 15200±200 cm^{-1}, characteristic of a d^9 ion in a tetragonal ligand field. This band may be assigned[12] to $^2A_{1g} \rightarrow {^2B_{1g}}$ and its broadness is expected for the CuO_6 chromophore because of the Jahn-Teller distortion in tetragonal field.

Magnetic moment of all these derivatives have been measured at room temperature and the results indicate that all the complexes show a magnetic moment in the range 1.38-1.49 B.M. The lower value of the magnetic moment in these complexes as compared to a spin-only value of 1.73 B.M. for a d^9 system is due to Cu – Cu interaction[13,14]. A slightly higher value of the magnetic moment of their alcoholate complexes may be indicative of the expected lesser Cu – Cu interaction due to the copper atoms being coordinated to the alcohol molecules.

Molecular weights and probable structure : Molecular weights of the above carboxylate derivatives have been determined ebullioscopically in refluxing chloroform and the values obtained (Table 1 and 2) show that copper mixed carboxylates, dicarboxylates as well as their alcohol adducts are dimeric in nature. Both the magnetic and spectral studies indicate that copper atoms in all the above derivatives are situated in a tetragonal environment. Although some direct experimental evidence is essential before a final view of structure can be arrived at, the dimeric structures suggested for copper acetate and its monohydrate[15,16] appear to be the most plausible ones for the above carboxylate derivatives as well as their mono-alcoholate complexes, respectively.

References

1. C. OLDHAM, *Prog. Inorg. Chem.*, 1968, **10**, 223.
2. C. D. GARNER and B. HUGHES, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 1.
3. J. CATTERICK and P. THORNTON, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 291.
4. R. J. DOEDENS, *Prog. Inorg. Chem.*, 1976, **21**, 209.
5. B. P. BARANWAL, G. K. PARASHAR and R. C. MEHROTRA, *Z. Naturforsch, Teil B*, 1979, **34**, 459.
6. D. C. BRADLEY, F. M. A. HALIM and W. WARDLAW, *J. Chem. Soc.*, 1950, 3450.
7. L. J. BELLAMY, "Infrared Spectra of Complex Molecules", Methuen, London, 1975, p. 190.
8. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds", Willey-Interscience, New York, 1970.
9 A. I. GRIGOREV, *Russ. J. Inorg. Chem.*, (*Engl. Transl.*), 1963, **8**, 409.
10 E. SPINNER, *J. Chem. Soc.*, 1964, 4217.
11. G. B. DEACON and R. J. PHILLIP, *Coord. Chem. Rev.*, 1980, **33**, 227.
12. A. B. P. LEVER, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.
13. B. N. FIGGIS and R. L. MARTIN, *J. Chem. Soc.*, 1956, 3837
14. A. P. GINSBERG, *Inorg. Chim. Acta Rev.*, 1971, 45.
15. G. M. BROWN and R. CHIDAMBARAM, *Acta Cryst. allogr.*, 1973, **B29**, 2393.
16. P. DE MEESTER, S. R. FLETCHER and A. C. SKAPSKI, *J. Chem. Soc., Dalton Trans.*, 1973, 2575.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 926-929

Gold Drugs

KAILASH C. DASH

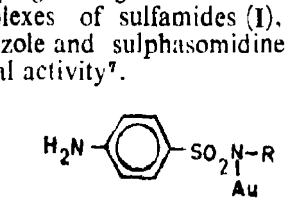
Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar-751 004

Rheumatoid arthritis, a progressive disease involving destruction of joint cartilage tissue, has been controlled in many cases over the past fifty years by the parenterally administered gold(I) compounds, *e.g.* gold sodium thiosulphate, $Na_3Au(S_2O_3)_2$ (*Sanocrysin*); gold disodium thiomalate, Na_2Autm (*Myocrisin*); gold thioglucose, GTG (*Solganol*) and gold thiopolypeptides (*Aurodetoxin*). An orally administered form of gold, [(2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranosato-*S*)(triethylphosphine) gold] (*Auranofin*) is presently undergoing extensive clinical trial for the treatment of rheumatoid arthritis. Recent advances in biological, chemical and medical disciplines now provide better understanding of the processes whereby the gold complexes exercise their physiological and pharmacological effects, resulting in exciting new developments in their therapeutic applications.

ALTHOUGH living things have a natural requirement for some metal ions, gold, so far as is known, is not one of them. Metallic gold is exceptionally stable and has a low natural abundance. These factors alongwith the fact that living things have not developed a mechanism for converting metallic gold into a soluble form which can be used biochemically, are responsible for making gold not a natural requirement. The Chinese were the first, in 2500 B.C., to administer gold compounds to living beings to produce a therapeutic effect. In early days gold was regarded as a universal cure-all, favourably affecting the course of all diseases. This continued upto late eighteenth century but with no biochemical basis for such treatment. It is not surprising, therefore, that confidence in its use was low.

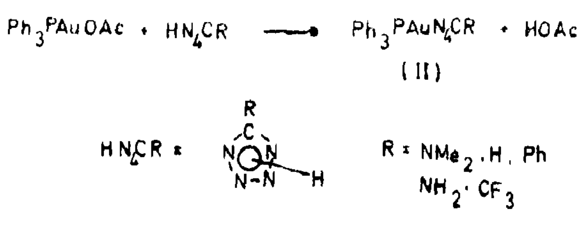
Gold cyanide, $KAu(CN)_2$, was observed by Koch[1] to inhibit the growth of *Tubercle bacilli* in the test tube and it is this incident which paved the way for the use of gold salts for the treatment of a number of pathogenic organisms including tuberculosis, syphillis, *etc.* and put gold therapy on a sound basis. The fortuitous use of gold complexes by Lande[2] and the improvement of articular manifestations in patients with tuberculosis and coincident rheumatoid arthritis, led Forestier[3] in 1929 to use such complexes specifically for the treatment of rheumatoid arthritis, although serious toxic and fatal reactions were associated. Subsequently, the use of gold-sulphur complexes was found to be safer though concern regarding their toxicity influenced their dosage and the frequency of administration. A carefully conducted multi-centred study by the Empire Rheumatism Council in the late 1950's established that gold was an effective agent with remittive potential[4]. Now, with increasing knowledge of modern pharmacokinetics and wider experience, gold therapy has become safer and more effective in the treatment of rheumatoid arthritis.

Gold salts and sodium aurosulphite, $Na_5Au(SO_3)_4.5H_2O$ are used against tuberculosis[5]. Gold drugs are preferred[6] for the treatment of the skin disease *Pemphigus vulgaris*, and *in vitro* tests using gold complexes of sulfamides (I), sulphadiazine, sulphamethizole and sulphasomidine show a higher antimicrobial activity[7].



(I)

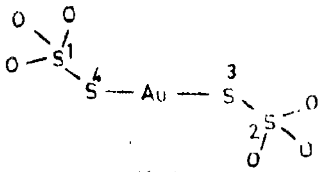
The antipyrine complex of gold $[AuCl_4][HL]$, has antitumer activities[8] as also the 5-substituted tetrazole triphenylphosphine gold(I) complexes[9](II). The antiarthritic drug, (2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranosato-*S*)(triethylphosphine)gold, auranofin is recently shown to have antitumor properties[10].



Gold drugs against arthritis: The antiarthritic activity of gold(I) compounds may be related to the high affinity, and hence selectivity, of Au^I for sulphydryl S as a biological ligand. It is notable that connective tissue diseases are often accompanied by subnormal levels of serum SH groups and the gold compounds (mainly thiols) in clinical use are potent inhibitors of sulphydryl-disulphide (SH-SS) exchange reactions[11] and can participate in facile sulphydryl ligand exchange reactions. Gold is now one of the

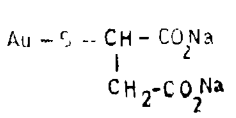
few drugs that can effectively alter the course of rheumatoid arthritis.

Gold sodium thiosulphate, $Na_3[Au(S_2O_3)_2]$, clinically known as Sanocrysin (**III**) has been used for the treatment of arthritis, tuberculosis and leprosy[11].

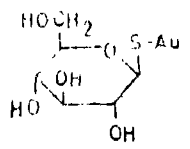


(III)

The drug is administered in aqueous solution through intramuscular or intravenous injections. Gold disodium thiomalate, Na_2Autm, (Myocrisin) (**IV**) has stood the test of the time in its use against arthritis. A suspension of this compound gives favourable results against chronic rheumatism. Administered parenterally, it suppresses both the primary and secondary lesions while increasing the Au levels, and is effective against adjuvant induced arthritis[12]. Gold thioglucose, GTG (Solganol) (V) is widely used against arthritis and seems to be less toxic than Na_2Autm.



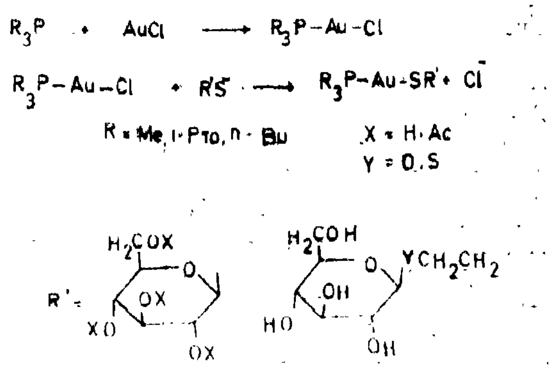
(IV)



(V)

A heavy dose (350-500 mg Au/kg body weight) of GTG induces hyperphagia (increased macrophage level), insatiable appetite and obesity in certain strains of mice, but in clinical dose (0.35 mg Au/kg) it is rather safe[13]. It is administered as an oil-suspension intramuscularly, and a depot effect is noticeable. Aqueous solutions of gold thiopolypetides are commercial drugs (Aurodetoxin). Although some patients can safely remain on gold therapy for many years, about 35 percent do suffer from some toxic side-reactions.

Oral gold drugs : Oral drugs are of value in permitting the administration of minimum daily doses and of facilitating the control of both dosage and related toxicity. The known soluble gold drugs given orally provide no protection against adjuvant arthritis and the need for new gold drugs was great. In searching for new oral gold drugs, Sutton and coworkers[14] noted that alkylphosphine gold complexes, R_3PAuX, administered orally, were as effective as other antiinflammatory agents for adjuvant arthritis and harmful retention of gold by kidney is very much reduced. These compounds are highly soluble in lipids and their therapeutic responses seem to be structure-dependent. Although non-gold phosphine compounds gave no protection, comparative studies indicated that the nature of the phosphine ligand in the gold complexes played a greater role in bringing about changes in biological activity than did the other group (X) bonded directly to Au.

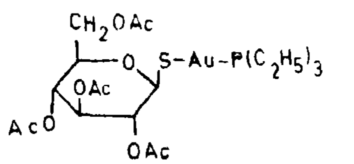


The serum gold levels, as well as the therapeutic effect, were highest with Et_3PAuCl and decreased with increasing bulkiness of the alkyl substituent (Table 1).

TABLE 1—SERUM GOLD LEVELS AND ANTIARTHRITIC PROPERTIES OF R_3PAuX COMPLEXES

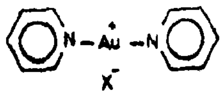
	Serum gold μm day 16	% Reduction of hind leg volume		
		Primary Lesion (injected leg)		Adjuvant arthritis (uninjected leg) day 16
		day-3	day 16	
Me_3PAuCl	8	10	—	—
Et_3PAuCl	27	14	28	37
$(i\text{-}Pr)_3$PAuCl	17	15	16	33
$(n\text{-}Bu)_3$PAuCl	5	20	—	—
Me_3PAuTG	12	14	16	—
Et_3PAuTG	21	17	—	27
$(i\text{-}Pr)_3$PAuTG	—	18	15	16
$(n\text{-}Bu)_3$PAuTG	6	28	—	—
Et_3PAupATG	21	30	30	45
$(n\text{-}Bu)_3$PAupATG	6	28	—	—

The data in Table 1 show that the highest antiarthritic activity for a constant X moiety (X = halide or sugar-containing thiolate) was obtained for the triethylphosphine complex, compared to the methyl, isopropyl and n-butyl analogues. For the triethylphosphine complexes, the greatest activity was for X = 2,3,4,6-tetraacetyl-β-D-1-thioglucose, which is undergoing chinical trial on human subjects[15]. This complex Et_3PAupATG (Auranofin) (**VI**) has proven much more satisfactory and in rats, oral doses of auranofin produced lower serum and kidney gold levels than the equivalent intramuscular injection of Na_2Autm, and the activity against induced adjuvant arthritis was great.

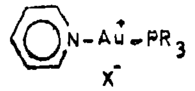


(VI)

It was suggested that small daily doses of auranofin maintain a more constant serum gold level and thereby avoid toxic reactions which are caused by large pulses of serum gold, following weekly or monthly Na_2Autm injections. The dose-related serum gold levels indicate that auranofin is effectively absorbed, and produces significant dose-response suppression of primary and secondary lesions of adjuvant arthritic rats and its antiarthritic potency is equal to or better than injectable Na_2Autm. Like Na_2Autm it produces systematic changes including alternation in the circulating antibodies, decreases in rheumatoid factor and increases in albumin levels[15]. Pharmacokinetic studies in normal rats suggest that daily oral chrysotherapy produces a greater stability in blood gold levels and less renal gold accumulation than injectable gold drugs. Auranofin, but not Na_2Autm inhibits lysosomal enzyme release (and/or decrease in immune complex formation) which explains its therapeutic action. A significant difference between Na_2Autm and auranofin is that Na_2Autm does not potentially inhibit the sulphydryl group reactivity. The predicted value of auranofin in rheumatoid arthritis based on the arthritic and immunological parameters in the *in vivo* and *in vitro* models is borne out in human studies[16].

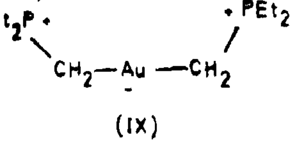


(VII)



(VIII)

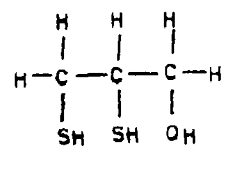
Among examples of some other orally administered gold drugs are the bis-coordinated gold(I) salts of the type $[R_3PAuPR'_3]^+X^-$, $(R_3PAu)_2S$, $[R^1R^2SAuSR^2R^1]^+ X^-$, $[Py\text{-}Au\text{-}Py]^+ X^-$ (VII) and $[Py\text{-}Au\text{-}PR_3]^+ X^-$ (VIII), (where $R = C_{1-4}$ alkyl or alkoxy, Ph, halophenyl, C_{1-4} alkoxyphenyl ; $X = ClO_4$, IO_4, BF_4 and PF_6) and a novel cyclic phosphorous ylide complex, $[Et_2PCH_2AuCH_2PEt_2]^+ Cl^-$ (IX).



(IX)

Gold poisoning and treatment : Most of the effective gold drugs are compounds of S and P containing ligands with Au^I. Pharmacological as well as toxicological studies preclude the use of gold(III) compounds as drugs. Gold(III) compounds are highly toxic, because of their strong oxidising power, greater inhibition of enzymes and greater retention in tissues.

An effective treatment of rheumatoid arthritis with gold drugs results in some degree of clinical toxicity whose severity and extent varies depending upon the mode of administration, the rate of elimination of gold from the body and other factors. The common toxic reactions involve the skin and mucous membrane. Because of their toxicity, gold drugs are not tolerated by aged individuals and by individuals having renal disease, infectious hepatitis, blood dyscrasias, urtricaria, eczema and colitis.



(X)

To avoid the serious toxic reactions, chrysotherapy is initiated with small doses of gold and the dose regimen is increased gradually. The therapy is withheld temporarily in case of a serious untoward response. When the toxic reactions are too severe, detoxifying agents (antagonists) such as penicillamine (β, β-dimethyl crysteine), dimercaprol (2,3-dimercaptopropanol, commonly known as British Anti-Lewisite, BAL) (X), antihistamines or adrenocorticosteroids are administered topically[17]. Clinical trials of dimercaptosuccinic acid (dms) as an antagonist have recently been suggested[18]. It is more water-soluble and less lipid-soluble than BAL, and should favour excretion rather than distribution. These antagonists have the property of reacting with gold to form the tightly bound complexes thereby preventing or reversing the binding of the toxic gold to body ligands, and promoting excretion of gold through urine or faeces.

Conclusion :

The rich coordination chemistry of gold gives rise to a biochemistry that is potentially very complicated. Nevertheless, a wide variety of both physical and chemical techniques are now being applied to this problem to understand the difference in behaviour between the intramuscular and oral gold drugs. Preferred gold drugs are compounds of gold(I). Gold(III) is too toxic to act as a drug. Gold(I) seems to follow the sequence given below as it is distributed through the body and excreted.

Injection site (Na_2Autm, GTG,...) —— → Blood stream ← ⇌ Liver — faeces; ⇌ Kidneys — urine; ⇌ Other tissues; ⇌ Site of therapeutic action
Stomach and intestine (Et_3PAuCl, $Et_3PAupATG$) —— → Blood stream

Gold-sulphur complexes are more effective and remittive agents for the treatment of rheumatoid arthritis. They are also beneficial in the treatment of psoriatic arthritis and discoid lupus, pemphigus vulgaris and bronchial asthama. A new compound, auranofin, in which gold is stabilised by both sulphur and phosphorous ligands, is shown to have several advantages over conventional gold-sulphur complexes. The hydrophobic and non-ionic characteristic of auranofin facilitate cell membrane penetration

and thus it is effective at lower blood concentrations, thereby avoiding the serious adverse reactions of gold-sulphur drugs.

The therapentic potential of the gold complexes is significant and further investigation in this area should be stimulating not only for the treatment of rheumatoid arthritis but also for that of a number of other diseases[19,20].

References

1. R. Koch, *Deut. Med. Woch.*, 1890, **16**, 756.
2. K. Lande, *Münch. Med. Woch.*, 1927, **74**, 1132.
3. J. Forestier, *Bull. Mém. Soc. Méd. Hop (Paris)*, 1929, 53, 323.
4. Empire Rheumatism Council, *Ann. Rheum. Dis.*, 1960, **19**, 95.
5. B. Oddo, *Arch. Farmacol. Sper.*, 1927, **44**, 141.
6. N. S. Pennys, W. E. Eaglestein and P. Frost, *Arch. Dermatol*, 1973, **108**, 56.
7. S. Yamashita, Y. Sayema and I. Nishikawa, *Experientia*, 1978, **34**, 472.
8. D. G. Craciunescu, *An. R. Acad. Farm.*, 1977, **43**, 265.
9. R. L. Kirby, W. M. Peterson, G. L. Blundell, S. Horton, R. A. Henry and H. B. Jonassen, *Inorg. Chem.*, 1976, **15**, 1721.
10. T. M. Simon, D. H. Kunishima, G. J. Vibert and A. Lorber, *Cancer*, 1979, **44**, 1965.
11. B. H. Freyberg, W. D. Block and S. Levey, *J. Clin. Investigation*, 1941, 20, 401.
12. D. T. Walz, M. J. DiMartino and A. Misher, *Ann. Rheum. Dis.*, 1971, **30**, 303.
13. G. Brecher and S. H. Waxler, *Am. J. Physiol.*, 1950, **162**, 428.
14. B. M. Sutton, E. McGusty, D. T. Walz and M. J. DiMartino, *J. Med. Chem.*, 1972, **15**, 1095.
15. F. -E Berglof, K. Berglof and D. T. Walz, *J. Rheumatol.*, 1978, **5**, 68.
16. A. E. Finkelstein, F. R. Roisman and D. T. Walz, *Inflammation*, 1977, **2**, 143.
17. D. F. Hill, *Med. Clin. N. Am.*, 1968, **52**, 733.
18. J. H. Graziano in "Clinical Chemistry and Toxicology of Metals", ed. S S. Brown Elsevier, North Holland, 1977, p. 608.
19. K. C. Dash and H. Schmidbaur in "Metal Ions in Biological System", ed. H. Sigel, Marcel Dekker, New York, 1982, Vol. 14, p. 179.
20. K. C. Dash and H. Schmidbaur, unpublished work.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 930-935

Polarographic Study of Complexes of Cadmium(II) and Lead(II) with Ethoxyacetate Ions

RAM PARKASH*, S. K. REHANI and RENU BALA

Department of Chemistry, Panjab University, Chandigarh-160 014

Reduction of the complexes of cadmium(II) and lead(II) at d.m.e. in aqueous and aqueous-methanol media at μ = 1.0 M ($NaClO_4$) at 15±0.1 and 25±0.1° is reversible and diffusion-controlled. Four complex species are formed in either case. The overall stability constants of 1 : 1, 1 : 2, 1 : 3 and 1 : 4 complexes have been determined by DeFord and Hume, and Mihailov's mathematical treatment. Lead(II) complexes have been found to be much stronger than the corresponding cadmium(II) complexes. Thermodynamic parameters have been determined. Percentage distribution of cadmium(II) and lead(II) present in various forms in equilibrium as a function of the ligand concentration have been calculated.

RECENTLY, complexes of certain plant auxins and fungicides with trace elements, cadmium(II), zinc(II), manganese(II) and thallium(I) have been reported[1,2]. In the present investigation, the interaction of ethoxyacetate, a fungicide, with trace elements cadmium(II) and lead(II) at d.m.e. in aqueous and aqueous-methanol media has been studied. Thermodynamic parameters and percentage distribution of metal ions present in various forms in equilibrium as a function of logarithm of ethoxyacetate concentration have also been calculated.

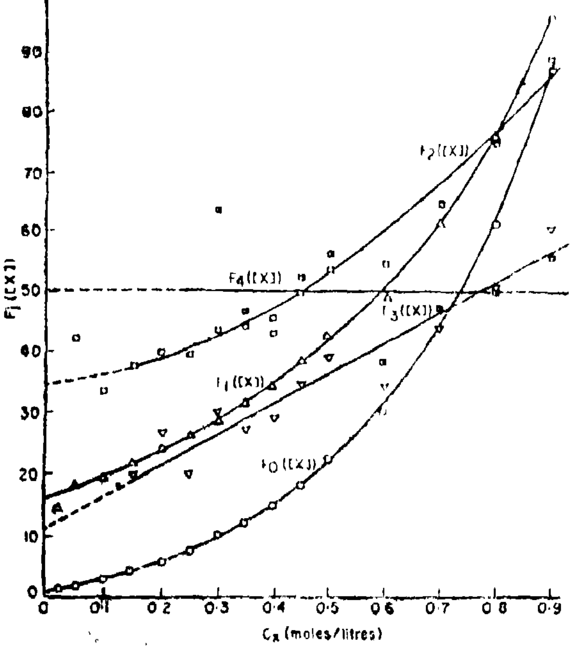


Fig. 1. Plot of $F_j([X])$ functions vs C_x for cadmium(II)-ethoxyacetate system in aqueous medium at 25±0.1°.

Experimental

Reagents : Cadmium nitrate tetrahydrate (E.M., A.G.), lead nitrate (B.D.H., AnalaR), sodium perchlorate monohydrate (E.M., G.R.), perchloric acid (Reidel) and Triton-X-100 (Rohm and Haas) were used as such. All the other chemicals used were of guaranteed purity. Triple-distilled mercury and double-distilled water were used in all the manipulations. Methanol was purified and distilled before use[3]. Ethoxyacetic acid was prepared from sodium ethoxide and freshly distilled chloroacetic acid[4], and purified by distillation under reduced pressure (109-111°/17 mm), b.p. 205-6°. Structure and purity of the acid was further confirmed by its pmr spectrum.

Solutions : Stock solutions of cadmium(II) and lead(II) were prepared in water and standardised[5]. Sodium salt of ethoxyacetic acid was prepared and

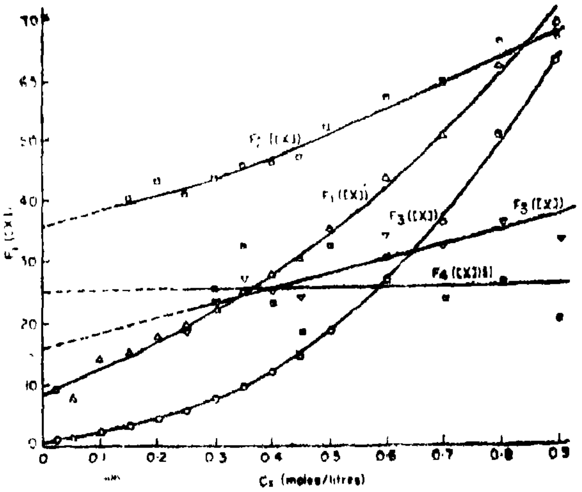


Fig. 2. Plot of $F_j([X])$ functions vs C_x for cadmium(II)-ethoxyacetate system in aqueous medium at 15±0.1°.

* Pro-Vice-Chancellor, Kurukshetra University, Kurukshetra-132 119.

TABLE 1—POLAROGRAPHIC DATA OF INTERACTION OF CADMIUM(II) AND LEAD(II) WITH ETHOXYACETATE IONS

$Cd^{II} = Pb^{II} = 4 \times 10^{-4}$ *M*, $\mu = 1$ *M* ($NaClO_4$), *p*H = 6.8 ± 0.1

C_x *M*	I $E_{\frac{1}{2}}$ −V	I i_{d_s}/i_{d_c}	II $E_{\frac{1}{2}}$ −V	II i_{d_s}/i_{d_c}	III $E_{\frac{1}{2}}$ −V	III i_{d_s}/i_{d_c}	IV $E_{\frac{1}{2}}$ −V	IV i_{d_s}/i_{d_c}	V $E_{\frac{1}{2}}$ −V	V i_{d_s}/i_{d_c}	VI $E_{\frac{1}{2}}$ −V	VI i_{d_s}/i_{d_c}
0.00	0.5775	—	0.5865	—	0.5705	—	0.3760	—	0.3810	—	0.3790	—
0.02	0.5800	1.058	0.5885	1.008	0.5750	1.082	0.3875	1.025	0.3845	1.107	0.3850	1.070
0.05	0.5850	1.061	0.5905	1.007	0.5800	1.071	0.3990	1.086	0.3990	1.269	0.3943	1.123
0.10	0.5900	1.107	0.5970	1.029	0.5865	1.122	0.4065	1.112	0.4045	1.286	0.4030	1.181
0.15	0.5945	1.127	0.6000	1.094	0.5913	1.162	0.4125	1.211	0.4145	1.297	0.4110	1.171
0.20	0.5983	1.145	0.6040	1.104	0.5945	1.162	0.4178	1.197	0.4175	1.339	0.4180	1.228
0.25	0.6015	1.149	0.6070	1.108	0.5980	1.260	0.4230	1.200	0.4230	1.285	0.4218	1.242
0.30	0.6048	1.157	0.6095	1.184	0.6020	1.238	0.4270	1.232	0.4260	1.365	0.4265	1.256
0.35	0.6075	1.157	0.6128	1.165	0.6053	1.246	0.4305	1.240	0.4305	1.365	0.4308	1.302
0.40	0.6090	1.263	0.6148	1.220	0.6085	1.234	0.4330	1.365	0.4335	1.445	0.4340	1.314
0.45	0.6115	1.295	0.6170	1.241	0.6115	1.307	0.4368	1.350	0.4370	1.445	0.4375	1.314
0.50	0.6138	1.331	0.6195	1.290	0.6140	1.384	0.4385	1.398	0.4405	1.461	0.4405	1.414
0.60	0.6175	1.346	0.6240	1.297	0.6195	1.411	0.4445	1.399	0.4445	1.515	0.4468	1.390
0.70	0.6220	1.378	0.6270	1.371	0.6235	1.626	0.4490	1.546	0.4485	1.627	0.4508	1.518
0.80	0.6255	1.471	0.6305	1.440	0.6300	1.519	0.4585	1.557	0.4550	1.578	0.4565	1.499
0.90	0.6300	1.471	0.6335	1.412	—	—	0.4580	1.578	0.4580	1.680	—	—

I Cadmium(II)-ethoxyacetate in aqueous medium at 25 ± 0.1°.
II Cadmium(II)-ethoxyacetate in aqueous medium at 15 ± 0.1°.
III Cadmium(II)-ethoxyacetate in 10% methanol medium at 25 ± 0.1°.
IV Lead(II)-ethoxyacetate in aqueous medium at 25 ± 0.1°.
V Lead(II)-ethoxyacetate in aqueous medium at 15 ± 0.1°.
VI Lead(II)-ethoxyacetate in 10% methanol medium at 25 ± 0.1°.

*p*H of this stock solution was adjusted using an Elico *p*H meter model LI-10. Solutions containing metal ions (4×10^{-4} *M*) and varying concentrations of complexing agent (0-0.9 *M*) were prepared in water and 10% methanol media at ionic strength 1 *M* maintained with sodium perchlorate.

The capillary characteristics measured in 0.1 *M* sodium perchlorate (open circuit) and at a mercury height of 60 cm were m = 2.012 mg sec^{-1} and t = 3.9 sec. Purified N_2 gas presaturated with the back-

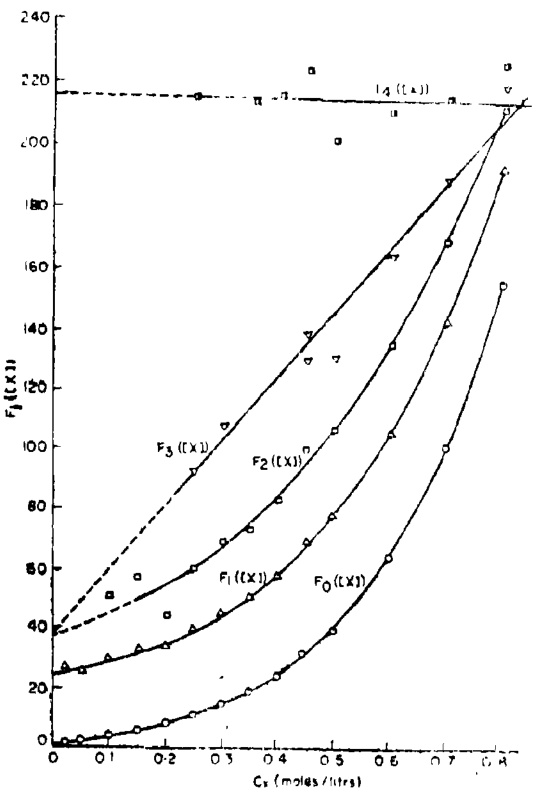


Fig. 3. Plot of $F_j([X])$ functions *vs* C_x for cadmium(II)-ethoxyacetate system in 10% methanol medium at 25 ± 0.1°.

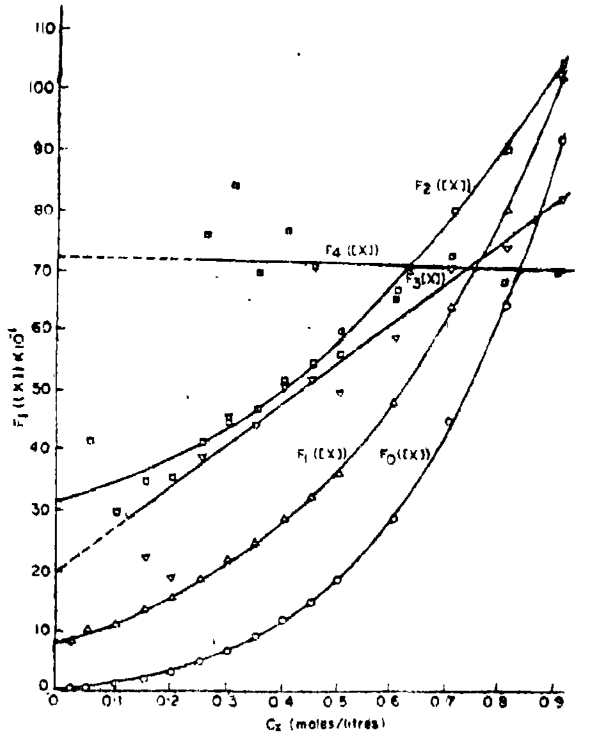


Fig. 4. Plot of $F_j([X])$ functions *vs* C_x for lead(II)-ethoxyacetate system in aqueous medium at 25 ± 0.1°.

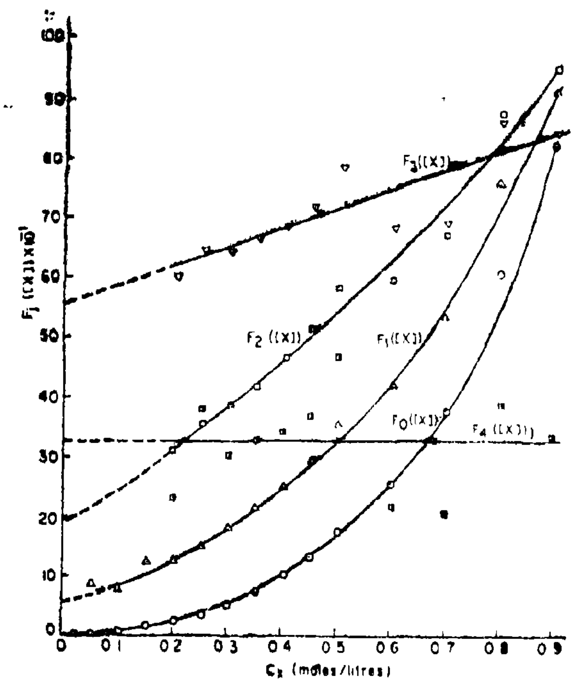


Fig. 5. Plot of $F_j([X])$ functions *vs* C_x for lead(II)-ethoxyacetate system in aqueous medium at 15±0.1°.

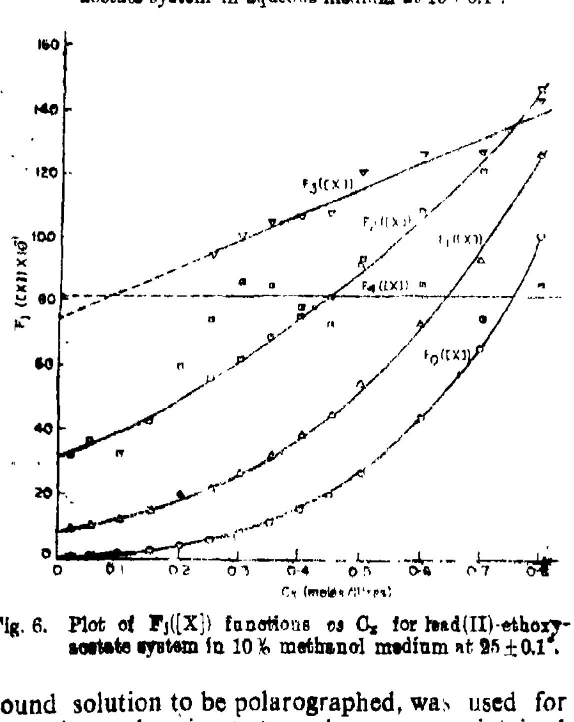


Fig. 6. Plot of $F_j([X])$ functions *vs* C_x for lead(II)-ethoxyacetate system in 10% methanol medium at 25±0.1°.

ground solution to be polarographed, was used for deaeration and an inert atmosphere was maintained over the solution during electrolysis. The electrolysis was carried out in a H-cell in conjunction with an agar-agar plug saturated with sodium chloride. Polarograms of 0.4 m*M* cadmium(II) and lead(II) solutions were obtained in the presence of different concentrations of ethoxyacetate at 15±0.1 and 25±0.1° using Radelkis model OH-102 polarograph in aqueous and 10% methanol media. Triton-X-100 (0.002% in the final solution) was used as maxima

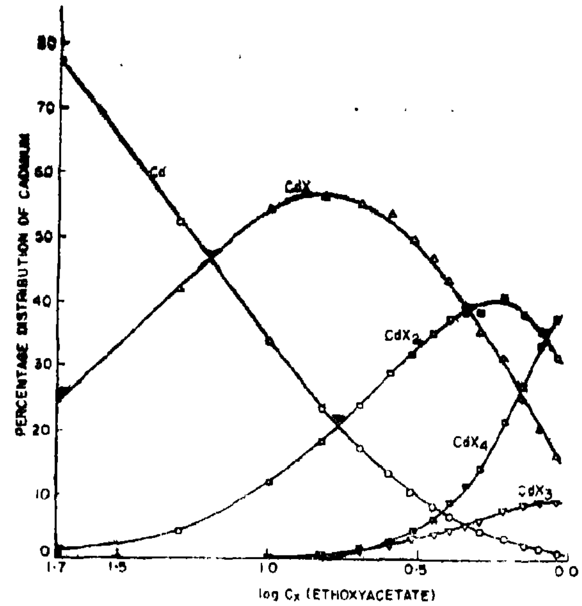


Fig. 7. Percentage distribution of cadmium in various forms as a function of −log C_x in aqueous medium at 25±0.1°.

suppressor whenever required. An iR compensation was used while working with methanolic solutions. The currents were corrected for residual current. The resulting polarographic data as a function of the ligand concentration (C_x), which was calculated from the *p*H of the solution and *p*ka value of the ligand (*p*ka = 3.84±0.03)[6], are given in Table 1.

Results and Discussion

Both cadmium(II) and lead(II) give single well-defined reversible polarographic reduction wave. Current is directly proportional to $\sqrt{h_{eff}}$, showing that the reduction is diffusion-controlled. Plot of $E_{d.e.}$ *vs* log i/id-i is a straight line with a slope of 31±2 mV. Cathodic reduction of cadmium(II) and lead(II) in ethoxyacetate is, therefore, reversible and involves two electron transfer in either case. That $E_{1/2}$ is independent of h_{eff} is in keeping with the reversible character of the wave. The shift in $E_{1/2}$ to more negative potential and decrease in the diffusion current with increase in ethoxyacetate concentration suggest complex formation. The data were analysed for the Fronaeus functions, $F_j([X])$, using DeFord and Hume expression[7].

The $F_j([X])$ functions thus calculated at different concentrations of the ligand are then solved for the stability constant by a graphical procedure (Figs. 1-6). Plots of $F_0([X])$, $F_1([X])$ and $F_2([X])$ against C_x are smooth curves, while $F_3([X])$ gives a straight line with slope and $F_4([X])$ a straight line parallel to the abscissa confirming the formation of four consecutive complexes, 1 : 1, 1 : 2, 1 : 3 and 1 : 4 in

TABLE 2—STABILITY CONSTANTS OF CADMIUM(II) AND LEAD(II) COMPLEXES WITH ETHOXYACETATE IONS

Complex species	Medium	Temp. ±0.1°	Overall stability constant of			
			Cadmium(II) complex		Lead(II) complex	
			DeFord-Hume method	Mihailov's method	DeFord-Hume method	Mihailov's method
MX_1	Aqueous	25	16.00	15.91	80.00	66.40
	Aqueous	15	9.00	9.52	60.00	66.97
	10% Methanol	25	24.00	24.77	80.00	90.48
MX_2	Aqueous	25	34.50	29.36	315.00	217.40
	Aqueous	15	36.00	20.69	190.00	192.60
	10% Methanol	25	37.00	58.45	322.00	291.12
MX_3	Aqueous	25	11.00	36.49	200.00	475.13
	Aqueous	15	15.80	29.98	555.00	369.28
	10% Methanol	25	38.00	91.96	750.00	624.79
MX_4	Aqueous	25	50.49	33.34	720.91	778.31
	Aqueous	15	25.67	32.57	326.39	581.02
	10% Methanol	25	215.35	108.50	813.44	1005.67

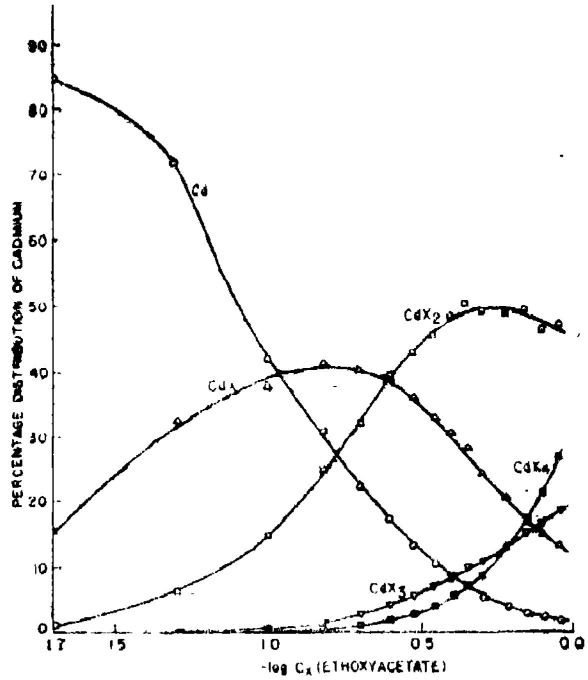


Fig. 8. Percentage function of cadmium in various forms as a function of $-\log C_x$ in aqueous medium at 15±0.1°.

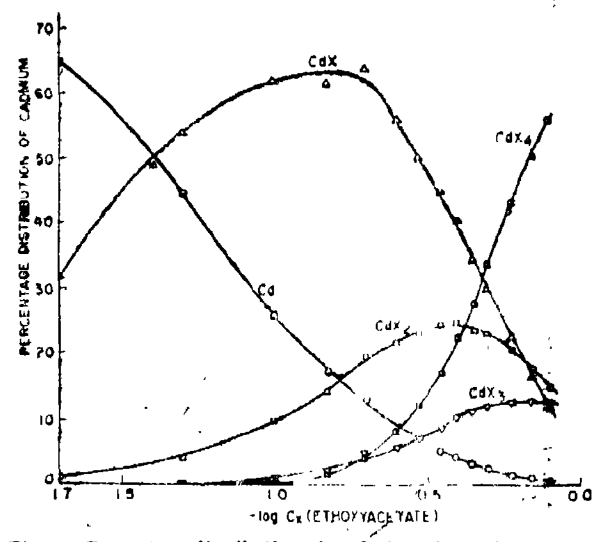


Fig. 9 Percentage distribution of cadmium in various forms as a function of $-\log C_x$ in 10% methanol medium at 25±0.1°.

equilibrium with each other in either case, having stabilities for cadmium(II)-ethoxyacetate complexes, $\beta_1=16.00$, $\beta_2=34.50$, $\beta_3=11.00$ and $\beta_4=50.49$, and for lead(II)-ethoxyacetate complexes, $\beta_1=80.00$, $\beta_2=315.00$, $\beta_3=200.00$ and $\beta_4=720.91$ in aqueous medium at 25±0.1°, respectively. The effect of temperature and medium on the stability of the complexes has been studied and the values are $\beta_1=9.00$, $\beta_2=36.00$, $\beta_3=15.80$ and $\beta_4=25.67$ in aqueous medium at 15±0.1° and $\beta_1=24.00$, $\beta_2=37.00$, $\beta_3=38.00$ and $\beta_4=215.35$ in 10% methanol medium at 25±0.1° for cadmium(II)-ethoxyacetate complexes, and $\beta_1=60.00$, $\beta_2=190.00$, $\beta_3=555.00$ and $\beta_4=326.39$ in aqueous medium at 15±0.1°, and $\beta_1=80.00$, $\beta_2=322.00$, $\beta_3=750.00$ and $\beta_4=813.44$ in 10% methanol medium at 25±0.1°, respectively (Table 2).

The complexity function, F_{calc}, at each data point and stability constant of the complexes formed are also determined by Mihailov's method[8] from the Mihailov's constants 'a' and 'A' and the results are presented in Table 2. There is a reasonably close agreement in the results obtained by the two methods for lead(II)-ethoxyacetate complexes. Although there is a difference between some of the stability constant values determined by the two methods for cadmium(II)-ethoxyacetate complexes, F_{calc} and F_{exp} values show a reasonably close agreement.

The thermodynamic parameters ΔH^0, ΔF^0 and ΔS^0 are calculated from the effect of temperature

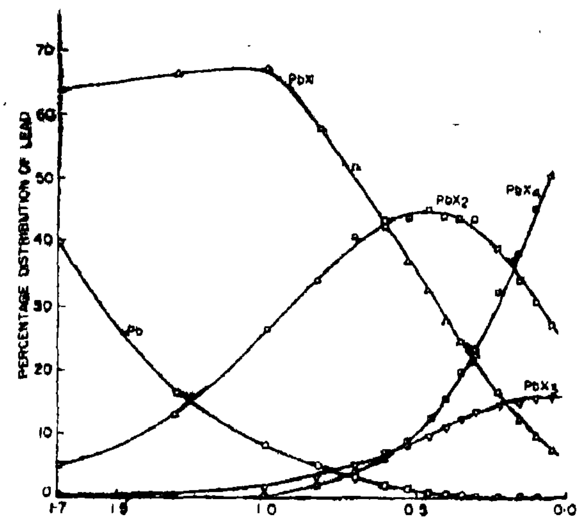


Fig. 10. Percentage distribution of lead in various forms as a function of $-\log C_x$ in aqueous medium at 25±0.1°.

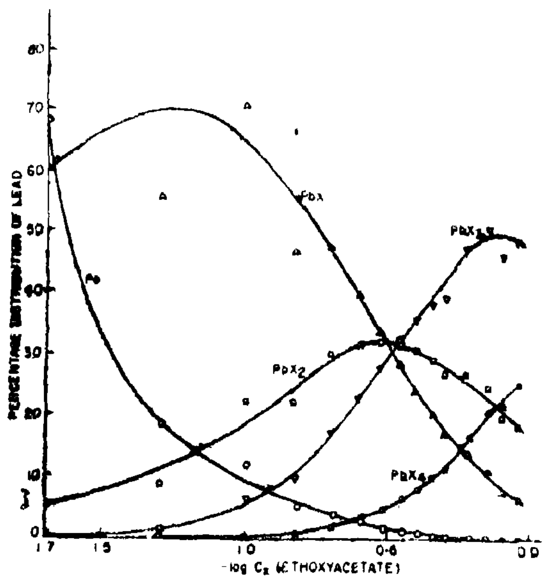


Fig. 11. Percentage distribution of lead in various forms as a function of $-\log C_x$ in aqueous medium at 15±0.1°.

on the stability constant of the complexes using equations :

$$\Delta H^{o} = -2.303\,RT_1T_2\,(\log\beta_{T_1} - \log\beta_{T_2})/(T_2 - T_1)$$

$$\Delta F^{o} = -2.303\,RT\,(\log \beta_j)_T$$

$$\Delta F^{o} = \Delta H^{o} - T\Delta S^{o}$$

and the results are presented in Table 3. The percentage distribution of the metal ions present in various forms in equilibrium as a function of ethoxyacetate concentration is also calculated and the results are presented graphically in Figs. 7-12.

It is evident from these results that the complexes formed are more stable at lower temperature or in aqueous methanol medium. However, the highest complex in general, becomes less stable on lowering the temperature. Also the complexes of lead(II) with ethoxyacetate are more stable than the corresponding cadmium(II) complexes. Lead(II)-ethoxyacetate complexes are also stronger than those of acetate[9]. Since ethoxyacetate is a considerably weaker base than acetate, the greater stability of the lead(II)-ethoxyacetate complexes may be reasonably ascribed to a certain degree of chelation.

Table 3—Thermodynamic Parameters for Complexation of Cadmium(II) and Lead(II) with Ethoxyacetate

Complex species	ΔF^{o} kJ mol^{-1}	ΔH^{o} kJ mol^{-1}	ΔS^{o} J deg^{-1} mol^{-1}
CdX_1	−6.87	+41.06	+160.85
CdX_2	−8.77	−3.04	+19.25
CdX_3	−5.94	−25.84	−66.78
CdX_4	−9.72	+48.28	+194.62
PbX_1	−10.86	+20.53	+105.84
PbX_2	−14.26	+36.08	+168.91
PbX_3	−18.18	−72.84	−200.88
PbX_4	−16.31	+56.55	+244.50

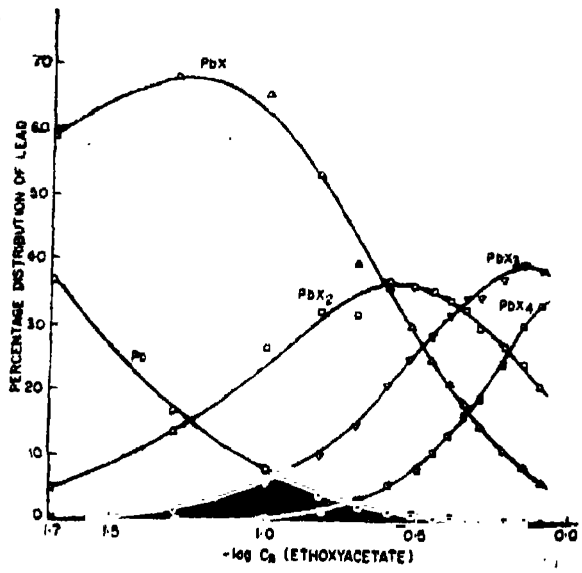


Fig. 12. Percentage distribution of lead in various forms as a function of $-\log C_x$ in 10% methanol medium at 25±0.1°.

Acknowledgement

One of the authors (R.B.) is thankful to the U.G.C., New Delhi for the award of a Senior Research Fellowship.

References

1. R. PARKASH, B. SINGH and R. BALA, *Trans. SAEST*, 1981, **16**, 141 ; *J. Indian Chem. Soc.*, 1983, **60**, 92.
2. R. PARKASH, S K. REHANI and R. BALA, *Proc. Indian Acad. Sci.*, 1984, **93**, 69.
3. A. I. VOGEL, "A Text Book of Practical Organic Chemistry", Longmans Green, New York, 1959.
4. A. H. BLATT, *Org. Synth.*, 1946, **2**, 260.
5. F. J. WELCHER, "Analytical Uses of Ethylenediaminetetraacetic Acid", Van Nostrand, 1959.
6. E. J. KING, *J. Am. Chem. Soc.*, 1960, **82**, 3575.
7. D. D. DEFORD and D. N. HUME, *J. Am. Chem. Soc.*, 1951, **73**, 5321.
8. M. H. MIHAILOV, *J. Inorg. Nucl. Chem.*, 1974, **36**, 107.
9. J. N. GAUR, R. C. MEHROTRA, M. M. PALRECHA, D. S. JAIN, A. KUMAR and C. M. GUPTA, *J. Polarogr. Soc.*, 1968, **14**, 122.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 936-939

Tetranuclear Metal Complexes of Copper(II) with *m*-Bis(1,3,5-trioxohexyl)benzene and *m*-Bis(1,3,5-trioxo-5-phenylpentyl)benzene and Corresponding Macrocyclic Schiff Base Complexes Formed with *o*-Phenylenediamine

A. K. JANA and B. SAHOO*

Department of Chemistry, Indian Institute of Technology, Kharagpur-721 302

Tetranuclear copper(II) complexes with the hexaketonate ions of *m*-bis(1,3,5-trioxohexyl)benzene (THB) and *m*-bis(1,3,5-trioxo-5-phenylpentyl)benzene (TPPB) have been isolated. Reaction of the metal complexes with *o*-phenylenediamine gives their respective tetranuclear macrocyclic complexes. The structures of the compounds have been established on the basis of infrared and electronic spectra. Cryomagnetic studies show that the compounds possess negative J values and are antiferromagnetic.

β-POLYKETONES and their metal complexes have been an exciting area of research during the last two decades[1-4]. Tri- and tetra-functional ketones, their anions and their Schiff bases have proved to provide essential conditions of geometry and potential abilities to coordinate towards one or two metal ions. Measurements of magnetic susceptibilities over a range of temperature have provided a powerful probe to find magnetic exchange and molecular structure for these chelates. Syntheses of naturally occurring organic compounds involving the polyketones *via* their metal complexes have been a fascinating area of research in recent years and metal ions are believed to play an important role in these stereospecific reactions.

Considerable effort has been made for the isolation of binuclear macrocyclic metal complexes involving Schiff bases of triketones with diamines. However, all attempts have been so far unsuccessful. The facile hydrolysis at the carbon-nitrogen bond and possibly the inadequate ring size appear to constitute important factors and preclude incorporation of two metal ions into the macrocyclic ring. In a recent communication we have reported[5] a series of tetranuclear nickel(II) complexes with hexaketones, *m*-bis-(1,3,5-trioxohexyl)benzene (*m*-THB) and *m*-bis (1,3,5-trioxo-5-phenylpentyl)benzene (TPPB).

In our continuing research in the area we report the tetranuclear copper(II) complexes of these hexaketones, their characterisation and spectral properties. Magnetochemical studies from ambient to 80 K reveal spin-spin interaction, and the exchange is antiferromagnetic. Reaction of the tetranuclear complexes with 1,2-diaminobenzene gives a large macrocyclic ligand, that houses four copper(II) ions. The demeric interactions are manifested through cryomagnetic studies.

Experimental

Chemicals used were of B.D.H. or S.M. quality. *m*-Bis(1,3,5-trioxohexyl)benzene and *m*-bis(1,3,5-trioxo-5-phenylpentyl)benzene were prepared as reported earlier[5].

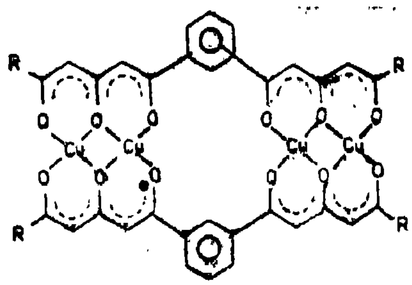
*Bis-[*m*-bis-(1,3,5-trioxonatehexyl)benzene]tetra copper(II), $Cu_4(C_{18}H_{14}O_6)_2$* : A solution of cupric chloride dihydrate (1.36 g, 0.004 mol) in methanol (60 ml) was added to *m*-bis-(1,3,5-trioxohexyl)benzene (0.66 g, 0.002 mol) in methanol (80 ml) followed by addition of a solution containing sodium hydroxide (0.32 g) in a minimum volume of water. A light green compound was formed readily and was refluxed for 1 h. The light green compound was filtered, washed with methanol and then by ether and finally dried in vacuum (Found : Cu, 28.7 ; C, 47.0 ; H, 2.80. $Cu_4(C_{18}H_{14}O_6)_2$ calculated Cu, 28.07, C, 47.68 ; H, 3.09%).

The deep green bis[*m*-bis-(1,3,5-trioxonato-5-phenyl-5-pentyl)benzene copper(II) was prepared in a similar manner (Found : Cu, 21.5 ; C, 57.20 ; H, 3.00. $Cu_4(C_{28}H_{18}O_6)_2$ calculated Cu, 22.01 ; C, 58.23 ; H, 3.11%).

Copper(II) complexes with the macrocyclic Schiff base ligand derived from the hexaketones and o-phenylenediamine. $Cu_4(C_{48}H_{30}O_8N_4).4H_2O$: A solution of cupric acetate monohydrate (0.8 g, 0.004 mol) in hot methanol was added to *m*-bis-(1,3,5-trioxohexyl)benzene (0.66 g, 0.002 mol) in hot methanol (80 ml) and the mixture was refluxed for 1 h. A solution of *o*-phenylenediamine (0.22 g, 0.002 mol) in methanol was added to it dropwise with constant stirring and the reflux was continued for 2 h more. During the course of the reaction colour of the compound changed from light green to deep green and finally to deep brown. The

product was filtered and washed with methanol and finally with ether and dried in vacuum (Found : Cu, 23.20 ; N, 4.80. $Cu_4(C_{48}H_{36}O_8N_4).4H_2O$ calculated Cu, 22.63 ; N, 99%).

The similar dark green macrocyclic complexes with TBPP and *o*-phenylenediamine was prepared in a similar way (Found : Cu, 17.69 ; N, 3.92. $Cu_4(C_{68}H_{44}O_8N_4).4H_2O$ calculated Cu, 18.54 ; N, 4.08%).



R = CH_3 or C_6H_5

Fig. 1

Results and Discussion

The tetranuclear copper(II)-hexaketonato complexes are readily formed in microcrystalline form by the reaction of the metal acetate or chloride with the respective ligands in methanolic or aqueous alcoholic solution. The *o*-phenylenediamine Schiff base complexes are conveniently obtained by refluxing the tetranuclear hexaketonato metal complexes in ethanol medium with the base in molar ratio 1 : 2.

Infrared spectra :

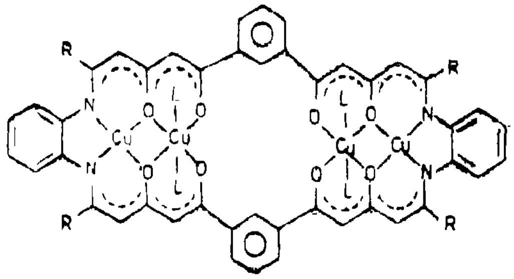
Hexaketonato copper(II) complexes : The hexaketones exhibit a broad and strong band near 3400 cm^{-1} in the region 3100-2700 cm^{-1} and two other medium intensity bands precisely located in the region 2650-2500 cm^{-1} which originate due to stretching vibrations of OH groups involved in intramolecular hydrogen bonding. In the copper(II) complexes the broad band in the region 3100-2600 cm^{-1} disappears implying break-down of the enolic OH bonds. A new broad band of medium to strong intensity, the centre of which lies near 3400 cm^{-1}, occurs in the spectra of the complexes on account of coordinated water.

In the fingerprint region the first strong band in the ligand appears near 1675 cm^{-1} which is characteristics of C=O stretching vibrations. In the copper(II) complexes this band shifts to about 1600 cm^{-1} on account of coordination. Apart from this band there are a number of vibrational bands that discern with CH_3 deformation, ring breathing vibrations of phenyl group in (TBPP) and CH out of plane vibrations and are not discussed here[6,7].

The structures of the complexes can be postulated as shown in Fig. 1, that are consistent with the important features of ir spectra. The postulated structure shows, that each hexaketonate ion acts as a polychelating agent coordinating towards a quadruplet of metal ions. The centres are constituted of two dimeric units linked through the central phenyl rings.

Schiff base complexes : The copper(II) complexes have a broad band near 3400 cm^{-1} which can be attributed to OH stretching vibrations of associated water. The complexes do not exhibit any band in the region 3300-3000 cm^{-1} which could be attributed to N−H stretching vibrations and indicate condensation of both the NH_2 groups of *o*-phenylenediamine with the metal ketonato complexes.

In the region 1600-1500 cm^{-1} the ir spectra show two bands near 1600 and 1550 cm^{-1} which from their intensity and sharpness can be assigned to C=O and C=N stretching vibrations, respectively. Vibrational bands in the region 1400-600 cm^{-1} resemble the general features of the spectra of free ketones. These spectral data manifest a macrocyclic quadrinuclear ring structure for the metal complexes where the terminal copper(II) ions are four-coordinated and planar with chromophore CuN_2O_2. Further evidences are obtained for their structures from electronic spectra and magnetic properties (Fig. 2).



R = CH_3 or C_6H_5 ; L = H_2O

Fig. 2

Electronic spectra :

The electronic spectral data are recorded in Table 1. The spectra of all the complexes show broad asymmetric bands in the region 13000-19000 cm^{-1} and in some cases can be resolved into two components. The asymmetric bands characterise d-d transitions of copper(II) ions, $^2E \rightarrow {}^2T_2$ and their split components under octahedral ligand fields with distortions or under planar arrangements with each copper ion coordinated to four donor atoms of ketonato ions and their macrocyclic Schiff bases. Electronic transitions beyond 20000 cm^{-1} are intense and are assigned to charge transfer transitions.

Magnetic properties :

The magnetic susceptibility data have been analysed in terms of Heisenberg-Dirac-Van Vleck spin-coupling Hamiltonian as adopted by Kambe. The data agree well with a dimeric model, and the inter dimer-dimer coupling has been considered to be zero. For a copper diad the energy levels for

TABLE 1—ELECTRONIC SPECTRA OF COPPER(II) COMPLEXES (cm^{-1})

Sl. no.	Ligand constituents	Formula of complexes	Ligand	Field bands	Charge transfer bands
1.	*m*-THB	$Cu_4(C_{18}H_{14}O_6)_2$	18400	16000	25000 29400
2.	TPPB	$Cu_4(C_{28}H_{18}O_6)_2$	18000	15800	24100 33250
3.	*m*-THB + *o*-phenylenediamine	$Cu_4(C_{48}H_{36}O_6N_4).4H_2O$	1	19000	29400
4.	TPPB + *o*-phenylenediamine	$Cu_4(C_{68}H_{44}O_6N_4).4H_2O$	—	18000	29000

$S_{12} = 1$ and 0 are $\frac{1}{2}$ J and 3/2 J, respectively where J is the exchange coupling constant. When the system is subjected to external magnetic field the energy levels are split further into $(2S_{12}+1)$ levels, *i.e.* the first order Zeeman term of $M_s g\beta H$ is to be added to the energy where g is the Lande splitting factor and Ms takes the value S_{12} to $-S_{12}$. The molar susceptibility is given by Van Vleck's equation,

$$\chi_M = \frac{N}{H}\left[\sum_i \frac{\delta E_i}{\delta H} \exp\left(-\frac{E_i}{kT}\right) \Big/ \sum_i \exp\left(-\frac{E_i}{kT}\right)\right]$$

and for the fact $g\beta H$ is small compared to kT in the range of temperature of interest, the susceptibility equation for copper diad is

$$\chi'_M = \frac{Ng^2\beta}{3kT} \times \frac{6 \exp^{(J/kT)}}{1 + 3 \exp^{(J/kT)}}.$$

The susceptibility of the compounds have been determined over the temperature range 300 to 80 K. The values given in Table 2 have been corrected for diamagnetism and Pascal's constants for all atoms and groups and for the temperature independant paramagnetism, N_α. The effective moment, μ_{eff} is given at each temperature using the equation, μ_{eff} 2.827 $[\chi'_m - N_\alpha)T]^{1/2}$. The value 60×10^{-6} cgs emu for copper(II) has been used for N_α.

TABLE 2—MAGNETIC SUSCEPTIBILITY OF COPPER(II)-HEXAKETONATES

m-THB			TPPB		
J = −280 cm^{-1},		g = 2.15	J = −205 cm^{-1},		g = 2.13
Temp. K	$\chi'_A \times 10^{-6}$ c.g.s., e.m.u.	μ_{eff} B.M.	Temp. K	$\chi'_A \times 10^{-6}$ c.g.s., e.m.u.	μ_{eff} B.M.
304	720	1.27	298	760	1.30
298	700	1.25	271	790	1.27
250	740	1.18	240	820	1.22
219	790	1.13	165	1023	1.14
201	830	1.11	142	1160	1.11
175	920	1.09	120	1280	1.09
148	1045	1.07	98	1540	1.08
112	1316	1.06	84	1790	1.07
80	1795	1.06			

The susceptibility data are found to agree well with the dimeric model (Tables 2 and 3) and indicate

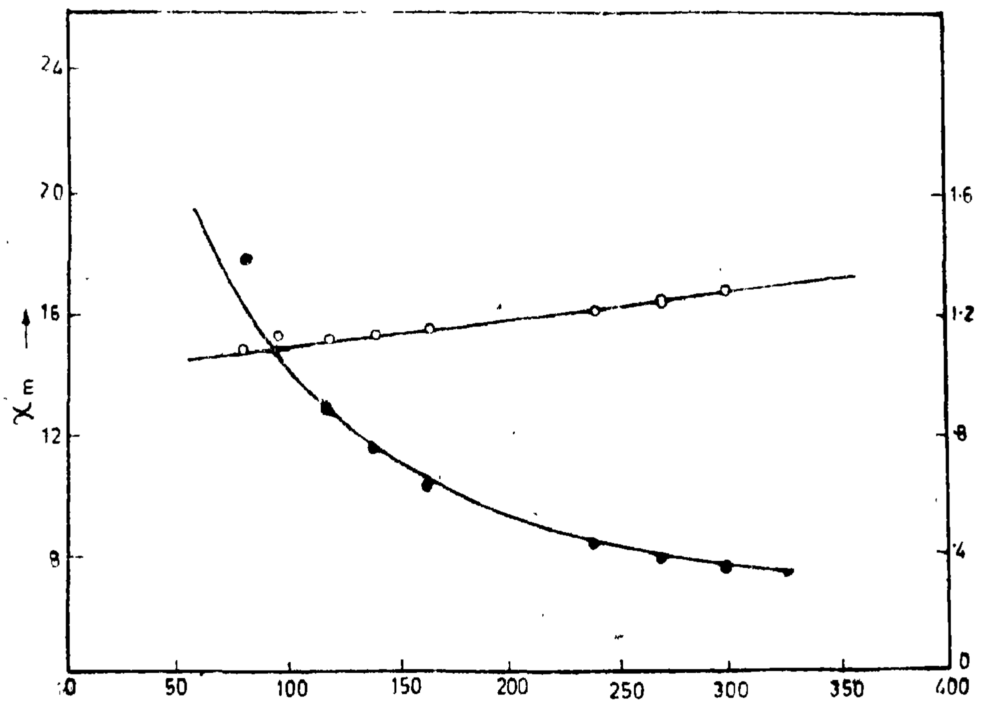


Fig. 8. Plot of χ'_m *vs* temperature and μ_{eff} *vs* temperature for $Cu_4(m\text{-THB})_2$.

Table 3—Magnetic Susceptibility of Copper(II)-macrocyclic Complexes

m-THB			TPPB		
$J=-265\ cm^{-1}$,		$g=2.2$	$J=-240\ cm^{-1}$,		$g=2.2$
Temp. K	$\chi'_A \times 10^{-6}$ c.g.s., e.m.u.	μ_{eff} B.M.	Temp. K	$\chi'_A \times 10^{-6}$ c.g.s., e.m.u.	μ_{eff} B.M.
305	503	1.10	300	690	1.20
290	513	1.08	248	748	1.17
272	512	1.04	205	890	1.18
242	585	1.01	169	950	1.10
210	578	0.96	138	1162	1.10
188	598	0.95	107	1540	1.12
149	745	0.93	83	1915	1.12
122	835	0.91			
89	1020	0.85			

that the dimer-dimer interactions through the bridging phenyl groups are weak. The values for ', the exchange coupling constant, and g, the Lande' splitting factor were calculated for each compound and are recorded in Table 2. The observed susceptibility data were compared with the predicted behaviour by curve fitting procedure (Fig. 3).

The magnetic moments of each compound are found to fall with decrease of temperature and the J values are negative. These results show that the spins of adjacent copper atom couple antiferromagnetically. The magnetic exchange interaction between the copper(II) ions are believed to occur through bridging oxygen atoms and the π system of β-polyketones, which have finite overlaps with the d orbitals of copper(II) containing the magnetic electrons. The results satisfy the proposed structures.

References

1. T. T. Howarth, G. P. Murphy and T. M. Harris, *J. Am. Chem. Soc.*, 1969, **91**, 517.
2. G. P. Murphy and T. M. Harris, *J. Am. Chem. Soc.*, 1972, **94**, 8258.
3. P. J. Wittek and T. M. Harris, *J. Am. Chem. Soc.*, 1973, **95**, 6865.
4. T. Yano, T. Ushijima, M. Sasaki, H. Kobayashi and K. Ueno, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2452.
5. A. K. Jana, N. P. Rath, B. Sahoo and B. Sahoo, *Indian J. Chem., Sect. A*, 1983, **22**, 371.
6. M. L. Miles, T. M. Harris and G. R. Hauser, *J. Am. Chem. Soc.*, 1963, **85**, 3884.
7. F. Sagar, H. Kobayashi and K. Ueno, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 794 ; 1973, **46**, 484.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 940-942

Copper and Silver Catalysed Oxidation of Glycinatopentaaminecobalt(III) by Potassium Perdisulphate

ANADI C. DASH, RABINDRA K. NANDA* and PRAKASH MOHANTY

Department of Chemistry, Utkal University, Bhubaneswar-751 004

The kinetics of oxidation of glycinatopentaaminecobalt(III) ion was investigated at 60° and 1 mol dm^{-3} perchlorate medium. The reaction is first order in [complex] and fractional order (0.5) in [peroxydisulphate]. Slight rate retardation is observed when $[H^+]$ increases from 0.1 to 0.7 mol dm^{-3}. The products of the reaction are Co^{II}, HCHO, CO_2 and NH_4^+. The reaction is catalysed by Ag^I and Cu^{II}. It is presumed that these catalysts produce species of their higher oxidation states which are more effective than peroxydisulphate. Increase in rate constants in presence of catalysts under nitrogen atmosphere is observed.

THE kinetics of metal ion catalysed peroxydisulphate oxidation of amino acids has been studied[1-3] from kinetic stand point. In this paper we report the kinetics of peroxydisulphate oxidation of coordinated glycinate (oxygen bonded) in $(NH_3)_5CoGlyH^{3+}$ in the presence of Ag^I and Cu^{II} ions under varying conditions.

Experimental

Potassium peroxydisulphate, perchloric acid, sodium perchlorate, copper sulphate and silver nitrate were of B.D.H., A.R. grade. Glycinatopentaaminecobalt(III) perchlorate was prepared by the reported method[3]. The reaction was studied under pseudo-first order conditions and the reaction was monitored by following the decrease of absorbance due to the complex with time at 500 nm using a Beckman DU2 spectrophotometer. The pseudo-first order rate constants were calculated from slopes of log (A_t-A_∞) *vs* time plots. Rate of production of Co^{II} was also followed by Kitson's method[4].

Results and Discussion

(i) The kinetic results can be summarised as follows.

The reaction was found to be fractional order (0.5) in [oxidant]. A plot of k_{obs} (Table 1) *vs* $[oxidant]^{\frac{1}{2}}$ was linear at constant $[Ag^+]$ and $[Cu^{2+}]$.

(ii) Under pseudo-first order condition, *i.e.* [oxidant] = 0.02 mol dm^{-3}, $[H^+]$ = 0.1 mol dm^{-3} and [catalyst] = 10^{-4} mol dm^{-3} the reaction followed first order kinetics in [complex]. Under these conditions, the first order rate constants remained constant ($0.64\times10^{-4}s^{-1}$) at different initial [complex] in the range 0.004 to 0.006 mol dm^{-3} using Cu^{II} ion as catalyst.

TABLE 1—EFFECT OF VARYING [OXIDANT] ON RATE OF OXIDATION OF COORDINATED GLYCINATE IN $(NH_3)_5CoGlyH^{3+}$ IN AQUEOUS MEDIUM

$[HClO_4]$ = 0.1 mol dm^{-3}, Ionic strength = 1 mol dm^{-3}, [complex] = 0.004 mol dm^{-3}, Temp. = 60°

$10^4[AgNO_3]$ mol dm^{-3}	$[K_2S_2O_8]$ mol dm^{-3}	10^4 k_{obs} s^{-1}	$10^4[CuSO_4]$ mol dm^{-3}	10^4 k_{obs} s^{-1}
1.0	0.016	0.680	1.0	0.590
1.0	0.020	0.750	1.0	0.689
1.0	0.030	0.840	1.0	0.727
1.0	0.040	0.900	1.0	0.729
1.0	0.050	0.940	1.0	0.806

(iii) The rate constant decreased with the increase in $[H^+]$. For example, under the conditions [complex] = 0.004 mol dm^{-3}, [oxidant] = 0.02 mol dm^{-3}, [catalyst] = 10^{-4} mol dm^{-3}, I = 1 mol dm^{-3}, and $[H^+]$ = 0.1 to 0.7 mol dm^{-3}, 10^4k_{obs} decreased from 0.64 to 0.50 s^{-1} for Cu^{II} catalysed reaction and 0.77 to 0.52 s^{-1} for Ag^I catalysed reaction.

(iv) Pseudo-first order rate constants were determined at various [catalyst]. The plot of rate constants against different [catalyst] was linear (Fig. 1). Rate constants at different initial [catalyst] are given in Table 2. k_{obs} *vs* $[M^{n+}]$, (M^{n+} = Ag^+ or Cu^{2+}), plot was linear upto 10^{-2} mol dm^{-3} for Cu^{II} catalysed reaction and upto 10^{-3} mol dm^{-3} for Ag^I catalysed reaction. The order in $[Ag^+]$ became greater than one at $[Ag^+] > 10^{-3}$ mol dm^{-3}.

(v) Rate constants followed by measuring decrease of $[Co^{3+}]_T$ and increase of $[Co^{2+}]$ were 0.64×10^{-4} and $0.63\times10^{-4}s^{-1}$ when [complex] = 0.004 mol dm^{-3}, $[Cu^{2+}]$ = 10^{-4} mol dm^{-3}, [oxidant] = 0.02 mol dm^{-3}, $[H^+]$ = 0.1 mol dm^{-3}, I = 1 mol dm^{-3} and temp. 60°. When the same experiments were conducted with Ag^I as catalyst the rate constants were 0.77×10^{-4} and $0.75\times10^{-4}s^{-1}$, respectively.

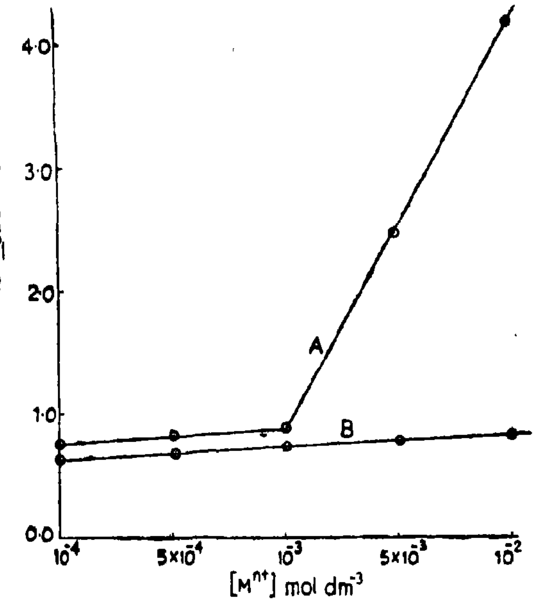


Fig. 1. 10^4 k_{obs} s^{-1} *vs* [M^{n+}] mol dm^{-3}; [complex]=0.006 mol dm^{-3}, [$HClO_4$]=0.1 mol dm^{-3}, [$S_2O_8^{2-}$]=0.03 mol dm^{-3}, I=1 mol dm^{-3}. A, [M^{n+}]=[Ag^+] and B, [M^{n+}]=[Cu^{2+}], all other conditions being the same.

TABLE 2—EFFECT OF VARYING [CATALYST] ON OXIDATION OF GLYCINATO COMPLEX

[$HClO_4$]=0.1 mol dm^{-3}, [oxidant]=0.02 mol dm^{-3}, [complex]=0.004 mol dm^{-3}, I=1 mol dm^{-3}, Temp.=60°

[$CuSO_4$] mol dm^{-3}	10^4 k_{obs} s^{-1}	[$AgNO_3$] mol dm^{-3}	10^4 k_{obs} s^{-1}
1×10^{-2}	0.83	1×10^{-2}	4.20
5×10^{-3}	0.78	5×10^{-3}	2.46
1×10^{-3}	0.73	1×10^{-3}	0.88
5×10^{-4}	0.68	5×10^{-4}	0.85
1×10^{-4}	0.64	1×10^{-4}	0.77

(vi) The oxidation reaction was studied under nitrogen atmosphere. The value of rate constant when [Ag^+]$_T$=10^{-4} mol dm^{-3}, [H^+]=0.1 mol dm^{-3}, [complex]=0.004 mol dm^{-3} and [$S_2O_8^{2-}$]=0.02 mol dm^{-3}, was $1.02\times10^{-4}s^{-1}$ while rate constant of the same reaction in air was $0.77\times10^{-4}s^{-1}$.

When the same experiment was conducted under nitrogen atmosphere taking copper as catalyst [Cu^{2+}]$_T$=10^{-4} mol dm^{-3}, the rate constant was $0.85\times10^{-4}s^{-1}$, the corresponding rate constant in air being $0.64\times10^{-4}s^{-1}$. Enhancement of rate constant under nitrogen atmosphere indicates that oxygen is an inhibitor.

Possible mechanism :

$$RGlyH^{3+} \underset{}{\overset{K_1}{\rightleftharpoons}} RGly^{2+} + H^+$$

$$+\ OX \qquad\qquad + M^{n+}$$

$$k_1 \downarrow \qquad K_2 \updownarrow$$

$$\text{product} \qquad RGly,M^{(n+2)+} + OX \xrightarrow{k_3} \text{product}$$

$$RGly^{2+} + OX \xrightarrow{k_2} \text{product}$$

where R=$(NH_3)_5Co^{3+}$, OX=oxidant, M^{n+}=Cu^{2+} or Ag^+, under pseudo-first order condition of [oxidant]$_T$ the rate law will be given by equation (1).

$$k_{obs} = \frac{k_1[H^+]+k_2K_1+k_3K_2K_1[M^{n+}]}{[H^+]+K_1+K_1K_2[M^{n+}]} \qquad (1)$$

Equation (1) can be linearised to equation (2) for which $k'_{obs}=k_{obs}$ at [M^{n+}]$_T$=0

$$\frac{(k_{obs}-k'_{obs})\{[H^+]+K_1\}}{[M^{n+}]\,K_1} = K_2k_3 - K_2k_{obs} \qquad (2)$$

At a fixed [M^{n+}], [oxidant]$_T$ and varying [H^+] the rate data were expressed by equation (2). Value of K_1 is negligible in comparison to [H^+], so equation (2) can be written as equation (3).

$$(k_{obs}-a)[H^+] = b - c\,k_{obs} \qquad (3)$$

where

$$a=k'_{obs},\ b=K_1K_2k_3\,[M^{n+}] \text{ and } c=K_1K_2\,[M^{n+}]$$

The plot of (k_{obs} − a) [H^+] *vs* k_{obs} for both Cu^{II} and Ag^I (both at 0.0001 mol dm^{-3}) catalysed reactions were linear (Fig. 2) supporting the proposed mechanism. The values of b and c for copper catalysed oxidation, were found to be 0.15×10^{-4} s^{-1} mol dm^{-3} and 2.0×10^{-1} mol dm^{-3}, respectively. The values of b and c for silver catalysed oxidation of the same complex are found to be 0.205×10^{-4} s^{-1} mol dm^{-3} and 0.25 mol dm^{-3}, respectively.

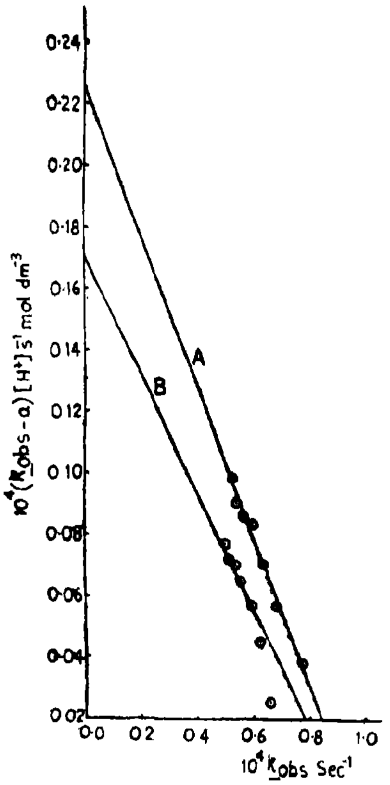


Fig. 2. 10^4 (k_{obs} − a) [H^+] s^{-1} mol dm^{-3} *vs* 10^4 k_{obs} s^{-1}. A, Ag^I catalysed reaction and B, Cu^{II} catalysed reaction.

The proposed reaction scheme for Ag^I and Cu^{II} catalysed oxidation reaction suggests that the

binuclear species are the reaction intermediates. Presumably Ag and Cu in such species exist in 2+ and 3+ states, respectively and induce inner-sphere oxidation of the coordinated glycinate. The observed order of the reaction with respect to $[S_2O_8^{2-}]$ being 0.5, $SO_4^{-\cdot}$ produced from the thermal dissociation of the oxidant $[S_2O_8^{2-} \rightleftharpoons 2SO_4^{-\cdot}]$ appear to be the oxidising species. At high [catalyst] deviation from the linearity of k_{obs} *vs* $[M^{n+}]$ plot is observed. The greater than first order dependance with respect to $[M^{n+}]$ suggests that presumably more than one catalyst metal ion are involved at higher concentration range. This point requires further study. Activation parameters for the copper and silver catalysed reaction were calculated by determining rate constants at four different temperatures (45, 50, 55 and 60°) and at $[H^+]=0.5$ mol dm^{-3}, $[Ag^+]=[Cu^{2+}]=10^{-4}$ mol dm^{-3} and $I=1.0$ mol dm^{-3}. The values of $\Delta H^{\ne}$ and $\Delta S^{\ne}$ for copper and silver catalysed reactions were found to be 42.12 kJ mol^{-1} and -206 Jk^{-1} mol^{-1}, and 28.7 kJ mol^{-1} and -241 Jk^{-1} mol^{-1}, respectively.

References

1. G. Chandra and S. N. Srivastava, *Indian J. Chem.*, 1973, **11**, 773.
2. M. G. Ram Reddy, B. Sethuram and T. N. Rao, *Indian J. Chem., Sect. A*, 1978, **16**, 31.
3. J. Fujita, T. Yasui and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1965 **83**, 654.
4. R. E. Kitson, *Anal. Chem.*, 1950 **22**, 664.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 943-945

Studies on Complexes of Copper(II) and Nickel(II) with Alkyl Xanthates and Their Mixed Chelates with Oxine and 2-Picolinic Acid

R. N. MURTY**, R. N. DASH** and D. V. RAMANA RAO*

Department of Chemistry, Regional Engineering College. Rourkela-769 008

Simple complexes of Cu^{II} and Ni^{II} with xanthates of isomeric alcohols of the composition ML_2 have been prepared, where L = isopropyl or isobutyl or isoamyl xanthate. These simple complexes on reacting with hetero donor ligands (X), like oxine and 2-picolinic acid in 1 : 1 molar ratio form mixed ligand complexes having general formula MLX. All these complexes have been characterised on the basis of chemical analyses, molar conductance, magnetic moment, and infrared and electronic spectral data. The magnetic and electronic spectral studies provide evidence for the existence of square planar structure for CuL_2, CuLX and NiL_2, and tetrahedral structure for NiLX.

SIMPLE and mixed metal xanthates are quite important as insecticides and fungicides[1] and they have found use in analytical separations, in vulcanisation of rubber[2], as antioxidents[3] and as lubricants[4]. A survey of literature reveals that some metal complexes involving only simple alkyl xanthates are reported. In view of the importance of this type of complex compounds it was, therefore, thought worthwhile to prepare complexes of some higher isomeric alkyl xanthates. The present study reports the preparation of copper(II) and nickel(II) complexes with isopropyl, isobutyl and isoamyl xanthates. Further, some mixed chelates using oxine and 2-picolinic acid have also been prepared.

Experimental

Potassium isopropyl, isobutyl and isoamyl xanthates were prepared and purified as reported in the literature[5]. Bis-isopropyl, isobutyl and isoamyl xanthates of Cu^{II} and Ni^{II} were prepared following the method reported earlier[6].

Reaction of bis-xanthato Cu^{II} and Ni^{II} with oxine or 2-picolinic acid: To a chloroform suspension of Cu^{II} or Ni^{II} xanthato complexes, a chloroform solution of oxine or 2-picolinic acid was added in 1 : 1 molar ratio. The resulting solution was refluxed for 2 h and the separated compound was suction-filtered, washed with ether and dried *in vacuo*.

Cu, Ni, C, N and S were estimated by standard methods. Infrared spectra in the range 4000-200 cm^{-1} were recorded at C.D.R.I., Lucknow. The magnetic susceptibilities were determined at room temperature on solid specimens using Gouy method. Diamagnetic corrections were made using Pascal's constants. The electronic spectra in $CHCl_3$ or acetone solution were recorded using Unicam SP 500 spectrophotometer. The molar conductance was measured in $\sim 10^{-3} M$ solution using Toshniwal CLO 102 conductivity bridge and a dip type cell.

Results and Discussion

The analytical, molar conductance and magnetic susceptibility data are recorded in Table 1. Infrared and electronic spectral data are recorded in Table 2.

As expected, all the compounds are found to be non-electrolytes and have very low molar conductance values. Magnetic moment measurements throw some light on the stereochemistry of these complexes. The μ_{eff} values of Cu^{II} simple and mixed chelates lie in the range 1.80-1.84 B.M. which is indicative of the presence of one unpaired electron as expected for a $3d^9$ cupric ion. It was reported earlier that magnetic moment values for tetrahedral Cu^{II} complexes are always higher ($\gg$2.0 B.M.) than the values for square planar complexes which lie nearer the spin-only value of $\sim$1.80 B.M. Thus, the observed values suggest that all the copper complexes are square planar involving $3d4s4p^2$ hybrid orbitals for bonding.

Simple Ni^{II} xanthates are essentially diamagnetic in nature indicating a square planar configuration. On the other hand, Ni^{II} mixed chelate complexes (NiLX) have magnetic moments in the range 3.12-3.22 B.M., indicating the presence of two unpaired electrons as expected for a tetrahedral configuration for Ni^{II} utilising $4s4p^3$ hybrid orbitals for bonding.

The molecular weight measurements carried out by Rast's camphor method indicate that all the complexes are monomeric in nature.

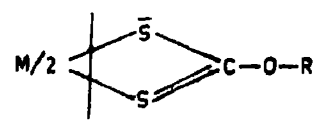
** Research and Control Laboratory, Rourkela Steel Plant, Rourkela-769 011.

TABLE 1—ELEMENTAL ANALYSES, MELTING POINT AND MAGNETIC SUSCEPTIBILITY DATA FOR Cu^{II} AND Ni^{II} SIMPLE AND MIXED CHELATES

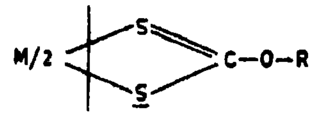
Sl. no.	Complex*	M.p. (°C)	μ_{eff} B.M.	Analysis % : Found/(Calcd.) M	C	N	S
1.	$Cu(IPX)_2$	172	1.80	19.16 (19.02)	28.56 (28.76)	—	38.24 (38.35)
2.	$Cu(IBX)_2$	165 d	1.82	17.35 (17.55)	33.02 (33.17)	—	32.75 (32.83)
3.	$Cu(IAX)_2$	159	1.82	16.45 (16.29)	37.12 (36.94)	—	32.75 (32.83)
4.	$Ni(IPX)_2$	127	Diamag.	17.63 (17.85)	28.95 (29.19)	—	39.20 (38.91)
5.	$Ni(IBX)_2$	140	Diamag.	16.28 (16.45)	33.56 (33.62)	—	—
6.	$Ni(IAX)_2$	99	Diamag.	15.32 (15.25)	37.62 (37.40)	—	—
7.	Cu(IPX)(OX)	250	1.82	18.56 (18.49)	45.72 (45.43)	4.15 (4.07)	18.78 (18.64)
8.	Cu(IBX)(OX)	180	1.84	17.86 (17.75)	—	4.02 (3.91)	18.12 (17.89)
9.	Cu(IAX)(OX)	189	1.88	17.24 (17.08)	48.26 (48.43)	—	—
10.	Cu(IPX)(Pyca)	176 d	1.84	20.02 (19.08)	37.64 (37.42)	4.45 (4.36)	20.45 (19.96)
11.	Cu(IBX)(Pyca)	208 d	1.82	18.66 (18.97)	—	4.26 (4.18)	19.26 (19.12)
12.	Cu(IAX)(Pyca)	205 d	1.83	18.42 (18.21)	41.18 (41.30)	3.92 (4.01)	—
13.	Ni(IPX)(OX)	250	3.20	17.14 (17.32)	46.25 (46.04)	4.26 (4.13)	18.64 (18.89)
14.	Ni(IBX)(OX)	182 d	3.14	16.82 (16.63)	47.24 (47.61)	—	18.26 (18.14)
15.	Ni(IAX)(OX)	250	3.22	16.22 (16.00)	49.28 (49.06)	3.92 (3.81)	—
16.	Ni(IPX)(Pyca)	250	3.12	18.26 (18.58)	37.82 (38.00)	—	20.15 (20.26)
17.	Ni(IBX)(Pyca)	250	3.20	17.05 (17.80)	39.85 (40.02)	4.46 (4.24)	19.62 (19.40)
18.	Ni(IAX)(Pyca)	250	3.22	17.02 (16.83)	42.04 (41.88)	4.16 (4.07)	—

* IPX = Isopropyl xanthate, IBX = Isobutyl xanthate, IAX = isoamyl xanthate, OX = oxine, Pyca = 2-picolinic acid.

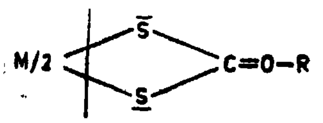
Infrared spectra : Alkyl xanthates are uninegative bidentate ligands and are bound to the metal ion through both its sulphur atoms. The structure of metal(II) xanthates can be represented as resonance hybrid of the three canonical forms, (A), (B) and (C).



(A)



(B)



(C)

Chatt *et al.*[7] have suggested that the resonance form (C) is of minor importance primarily because the infrared spectrum does not exhibit the $\nu_{C=O}$ band but a ν_{C-O} at ~1200 cm^{-1}. The resonance from (A) or (B) describes the most probable structure of metal(II) xanthates.

In the infrared spectrum of PIPX, PIBX and PIAX (free ligands), the ν_{C-O} band appeared in the range 1044-1135 and 1130-1170 cm^{-1}, whereas in simple xanthates and mixed xanthato complexes of Cu^{II} and Ni^{II}, the ν_{C-O} bands were observed in the range 1088-1170 and 1142-1200 cm^{-1}, respectively. These observations were in accord with the findings of Little *et al*[8].

In the free potassium alkyl xanthates, the $\nu_{C=S}$ appeared in the range 1040-1090 cm^{-1} and in complexes the band is shifted to a lower frequency and lies in the range 1005-1060 cm^{-1}. This lowering of the $\nu_{C=S}$ band indicated the involvement of sulphur in bonding with the metals[8].

In oxine complexes many bands due to oxine are found to be overlapping with the bands of xanthates. However, an additional characteristic band for ν_{C-O} was observed at ~1110 cm^{-1} which indicates the

TABLE 2—INFRARED AND ELECTRONIC SPECTRAL DATA (cm^{-1}) OF SIMPLE AND MIXED CHELATES OF Cu^{II} AND Ni^{II}

Sl. no.	Complex*	$\nu_{asy\ C-S}$	ν_{C-O}	ν_{M-N}	ν_{M-S}	λ_{max}
1.	$Cu(IPX)_2$	1015	1090 1142	—	405	15385
2.	$Cu(IBX)_2$	1035	1170 1200	—	400	15625
3.	$Cu(IAX)_2$	1040	1155 1200	—	395	15625
4.	$Ni(IPX)_2$	1021	1089 1152	—	397	20000, 23255
5.	$Ni(IBX)_2$	1045	1160 1182	—	400	20000, 23255
6.	$Ni(IAX)_2$	1040	1150 1170	—	390	20000, 23255
7.	Cu(IPX)(OX)	1028	1088 1158	325	410	15156
8.	Cu(IPX)(OX)	1038	1178 1200	335	410	14777
9.	Cu(IAX)(OX)	1035	1142 1195	330	395	15156
10.	Cu(IPX)(Pyca)	1008	1090 1150	338	395	14777
11.	Cu(IBX)(Pyca)	1038	1168 1190	333	390	14705
12.	Cu(IAX)(Pyca)	1035	1140 1192	335	410	14777
13.	Ni(IPX)(OX)	1032	1098 1142	310	410	11765, 15150
14.	Ni(IBX)(OX)	1042	1155 1175	300	390	11765, 15150
15.	Ni(IBX)(OX)	1035	1145 1178	300	410	11628, 15150
16.	Ni(IPX)(Pyca)	1022	1090 1150	295	385	11494, 14925
17.	Ni(IBX)(Pyca)	1025	1150 1170	300	390	11494, 15150
18.	Ni(IAX)(Pyca)	1025	1150 1170	310	385	11494, 15384

* Abbreviations as in Table 1.

presence of oxine group in the mixed chelate complexes as observed by earlier workers[9]. Further, the presence of additional bands due to picolinic acid in the mixed chelate complexes indicated its definite presence[10].

The metal-sulphur (M – S) bands for simple and mixed chelates of Cu^{II} and Ni^{II} appearing in the range 390-410 cm^{-1} (Table 2) confirmed the bonding of xanthate through sulphur atoms[11,12]. The metal-nitrogen (M – N) band for mixed complexes of Cu^{II} and Ni^{II} appeared in the range 295-338 cm^{-1} which gave direct evidence for the presence of oxine and picolinic acid bonded through nitrogen to the metal ion.

Electronic spectra : The electronic spectra of simple and mixed chelates of Cu^{II} show a broad band in the region 14500-16000 cm^{-1} which indicate square planar configuration for all the Cu^{II} complexes[13-15]. The simple chelates of Ni^{II} xanthates exhibit two medium bands or shoulders at ~20000 and ~23255 cm^{-1} indicating square planar environment around Ni^{II} with D_{4h} symmetry as observed by earlier workers[16,17]. For mixed chelate complexes of Ni^{II}, however, the bands were observed at ~15100 and ~11600 cm^{-1} which can be assigned to a tetrahedral environment around Ni^{II} as observed[18] earlier.

Acknowledgement

The authors (R.N.M. and R.N.D.) are highly thankful to the management of Rourkela Steel Plant, Rourkela for permission to publish this paper.

References

1. G. J. M. VANDERKERK and H. L. KLOPPING, *Recl. Trav. Chim. Pays-Bas*, 1952, **71**, 1179 ; *Nature (London)*, 1955, **176**, 808.
2. J. W. WARK and A. B. COX, *Trans. Am. I. M. M. E.*, 1946, **134**, 64.
3. D. COUCOUVANIS, *Prog. Inorg. Chem.*, 1970, **11**, 233.
4. R. EISENBERG, *Prog. Inorg. Chem.*, 1970, **12**, 295.
5. BAESSLER, KONRAD, FOLZGEORG, Ger. Pat. 1984/1971.
6. M. N. ANSARI, M. C. JAIN and W. U. MALIK, *J. Indian Chem. Soc.*, 1980, **57**, 861.
7. J. CHATT, A. L. DUNCANSON and M. L. NANANZI, *Suomen Kemi*, 1956, **29**, 75.
8. L. H. LITTLE, G. W. POLING and J. LEJA, *Can. J. Chem.*, 1961, **39**, 754.
9. R. C. CHARLES, H. FRIESER, R. FRIEDEL, L. E. HILLARD and W. D. JOHNSTON, *Spectrochim. Acta*, 1956, **8**, 1.
10. G. W. A. FOWLES, R. W. MATTHEWS and R. A. WALTON, *J. Chem. Soc. A*, 1968, 1108.
11. G. W. WATT and B. J. MCCORMICK, *Spectrochim. Acta*, 1965 **21**, 753.
12. R. A. WINOGRAD, D. J. LEWIS and S. J. LIPPARD, *Inorg. Chem.*, 1975, **14**, 2601.
13. L. SACCONI and M. CIAMPOLINI, *J. Chem. Soc.*, 1964, 278.
14. D. W. MEEK and S. A. EHRHARDT, *Inorg. Chem.*, 1965, **4**, 584.
15. A. B. P. LEVER, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968, p. 359.
16. C. K. JORGENSEN, *J. Inorg. Nucl. Chem.*, 1962, **24**, 1571.
17. G. MAKI, *J. Chem. Phys.*, 1958, **28**, 651 ; 1958, **29**, 1129.
18. S. SAMANTARAY and D. V. RAMANA RAO, *Indian J. Chem.*, 1974, **12**, 836.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 946-950

Metal Complexes with N^1-Benzoyl-N^2-(5-phenyl or 5-p-anisyl-1,3,4-oxadiazole-2-yl)thiocarbamide

K. C. SATPATHY*, B. B. JAL, R. MISHRA and (MRS.) S. PRADHAN

P. G. Department of Chemistry, Sambalpur University, Jyoti Vihar, Burla-768 017

The thiourea derivatives N^1-benzoyl-N^2-(5-phenyl-1,3,4-oxadiazole-2-yl)thiocarbamide (BPODTC) and N^1-benzoyl-N^2-(5-p-anisyl-1,3,4-oxadiazole-2-yl)thiocarbamide (BAODTC) are utilised for the preparation of Co^{II}, Ni^{II} and Cu^{II} complexes in ethanol medium. The structure of the complexes has been studied with the help of analytical and magnetic susceptibility data, uv and ir spectral measurements, conductometric and thermogravimetric analyses. The crystal field parameters of Co^{II} and Ni^{II} are also calculated. BPODTC acts as a bidentate ligand whereas BAODTC a tridentate one. $[M_2(BAODTC)_2X_4]$ and $[M(BPODTC)_2X_2]$, where $M=Co^{II}$, Cu^{II}, $X=Cl^-$, Br^-, NO_3^- and ClO_4^- have octahedral and distorted octahedral configurations, respectively, whereas $[Ni_2(BAODTC)_2X_4]$ is found to be octahedral and $[Ni(BPODTC)_2]X_2$ square planner in nature. Low molar conductance values in acetone except that of $[Ni(BPODTC)_2]X_2$ which is ionic, indicate that all these complexes are non-electrolytic.

METAL complexes with Schiff bases, derived by the condensation of 2-amino-5-substituted-1,3,4-oxadiazole with different aldehydes or ketones, are reported by us earlier[1-4]. Because of biological importance we have also synthesised a number of metal complexes with thiourea derivatives[5-11]. A survey of the literature reveals that there is no report on the synthesis of metal complexes with thiourea derivatives having 5-substituted-1,3,4-oxadiazole as one of the substituents in the thiourea moiety. In continuation of our studies on metal complexes having fungicidal properties, we report further the synthesis and structural elucidation of a few metal complexes with two thiourea derivatives, N^1-benzoyl-N^2-(5-phenyl-1,3,4-oxadiazole-2-yl)thiocarbamide (BPODTC) and N^1-benzoyl-N^2-(5-p-anisyl-1,3,4-oxadiazole-2-yl)thiocarbamide (BAODTC), which contain C=O, C=S and 5-substituted-1,3,4-oxadiazole groups.

Experimental

All the chemicals used were of B.D.H. or E.M. grade. The ligands N^1-benzoyl-N^2-(5-phenyl-1,3,4-oxadiazole-2-yl)thiocarbamide (pale yellow, m.p. 180°) and N^1-benzoyl-N^2-(5-p-anisyl-1,3,4-oxadiazole-2-yl) thiocarbamide (canary yellow, m.p. 176°) were synthesised by the reported method[12,13]. Ethanolic solution of the metal salt and the ligand in proper stoichiometric ratio were refluxed in ethanol for 2-3 h. The coloured precipitates appeared slowly during the reflux which were filtered, washed thoroughly with ethanol followed by ether and dried *in vacuo*. The complexes were insoluble in water but freshly prepared samples were sparingly soluble in ethanol, acetone, dioxane and benzene. The melting points of the complexes were not sharp and a few decomposed before melting. Based on the elemental analyses of the complexes by standard methods[14], the composition was proposed. The analytical data, and colour of the complexes are recorded in Table 1.

Physical measurements : The electronic spectra of the freshly prepared samples in dioxane and the vibrational spectra (KBr) were recorded on Beckman-35 and Perkin-Elmer 398 spectrophotometers, respectively. Magnetic susceptibilities were determined at room temperature by Gouy method employing $Hg[Co(CNS)_4]$ as standard. The necessary diamagnetic corrections were made using the literature values[15]. Thermal analyses of the complexes were carried out with Netzsch 429 simultaneous thermo analyser at a heating rate of 10° min^{-1} by taking 50 mg of the sample in each case. Conductance of the freshly prepared complexes in acetone solutions (10^{-3} M) were measured using a Toshniwal conductance bridge.

Results and Discussion

The ligands BPODTC and BAODTC can exist in different tautomeric intramolecularly hydrogen bonded forms as depicted in Figs. (1-4) (Y=H, OCH_3).

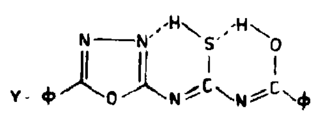


Fig. 1

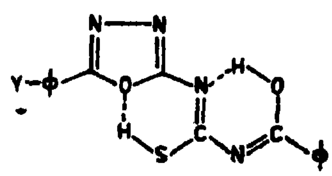


Fig. 2

TABLE 1—ANALYTICAL DATA

Complex	Colour M.p. °C	Analysis % : Found/(Calcd.) Sulphur	Nitrogen	Halogen	Metal
[Cu(BPODTC)$_2$Cl$_2$]	Buff, >250	8.07 (8.17)	14.28 (14.31)	8.99 (9.07)	8.05 (8.18)
[Cu(BPODTC)$_2$Br$_2$]	Yellow, 160 d	7.21 (7.34)	12.64 (12.84)	18.25 (18.35)	7.02 (7.22)
[Cu(BPODTC)$_2$(NO$_3$)$_2$]	Buff, >250	7.60 (7.65)	16.78 (16.75)	—	7.51 (7.61)
[Cu(BPODTC)$_2$(ClO$_4$)$_2$]	Buff, >250	7.21 (7.31)	12.69 (12.79)	8.01 (8.11)	7.07 (7.27)
[Cu$_2$(BAODTC)$_2$Cl$_4$]	Mimosa, 234	6.51 (6.54)	11.47 (11.46)	14.51 (14.52)	12.98 (13.02)
[Cu$_2$(BAODTC)$_2$Br$_4$]	Brown, >250	5.54 (5.53)	9.66 (9.69)	27.58 (27.69)	10.99 (11.01)
[Cu$_2$(BAODTC)$_2$(NO$_3$)$_4$]	Mimosa, >250	5.88 (5.90)	15.47 (15.50)	—	11.69 (11.75)
[Cu$_2$(BOADTC)$_2$(ClO$_4$)$_4$]	Grey, 250	5.11 (5.18)	9.01 (9.08)	11.31 (11.51)	10.22 (10.32)
[Co(BPODTC)$_2$Cl$_2$]	Purple, 99 d	8.19 (8.23)	14.32 (14.40)	9.09 (9.13)	7.44 (7.57)
[Co(BPODTC)$_2$Br$_2$]	Blue, 240	7.40 (7.38)	12.88 (12.92)	18.39 (18.45)	6.72 (6.79)
[Co(BPODTC)$_2$(NO$_3$)$_2$]	Green, >250	7.59 (7.70)	16.73 (16.85)	—	7.11 (7.08)
[Co(BPODTC)$_2$(ClO$_4$)$_2$]	Bluish green, 150 d	7.01 (7.06)	12.22 (12.37)	7.75 (7.83)	6.35 (6.50)
[Co$_2$(BAODTC)$_2$Cl$_4$]	Green, 206	6.82 (6.61)	11.49 (11.57)	14.56 (14.68)	12.08 (12.17)
[Co$_2$(BAODTC)$_2$Br$_4$]	Phiroza, 250 d	5.61 (5.59)	9.71 (9.77)	27.88 (27.92)	10.13 (10.28)
[Co$_2$(BAODTC)$_2$(NO$_3$)$_4$]	Red, >250	5.83 (5.96)	15.55 (15.64)	—	10.89 (10.96)
[Co$_2$(BAODTC)$_2$(ClO$_4$)$_4$]	Leaf brown, 110 d	5.15 (5.23)	9.08 (9.15)	11.51 (11.60)	9.57 (9.62)
[Ni(BPODTC)$_2$Cl$_2$]	Yellowish green, 237	8.19 (8.24)	14.35 (14.40)	9.11 (9.13)	7.46 (7.55)
[Ni(BPODTC)$_2$Br$_2$]	Yellowish green, >250	7.32 (7.38)	12.69 (12.92)	18.38 (18.46)	6.68 (6.77)
[Ni(BPODTC)$_2$(NO$_3$)$_2$]	Canary yellow, 250	7.68 (7.71)	16.79 (16.85)	—	7.00 (7.06)
[Ni(BPODTC)$_2$(ClO$_4$)$_2$]	Yellowish green, >250	7.12 (7.06)	12.25 (12.37)	7.78 (7.84)	6.36 (6.48)
[Ni$_2$(BAODTC)$_2$Cl]	Pale yellow, >250	6.59 (6.61)	11.42 (11.58)	14.70 (14.68)	12.05 (12.13)
[Ni$_2$(BAODTC)$_2$Br$_4$]	Marine grey, >250	5.60 (5.59)	9.68 (9.78)	27.88 (27.94)	10.12 (10.25)
[Ni$_2$(BAODTC)$_2$(NO$_3$)$_4$]	Pale yellow, >250	5.89 (5.96)	15.53 (15.66)	—	10.88 (10.94)
[Ni$_2$(BAODTC)$_2$(ClO$_4$)$_4$]	Marine grey, 210 d	5.18 (5.23)	9.07 (9.15)	11.55 (11.61)	9.55 (9.60)

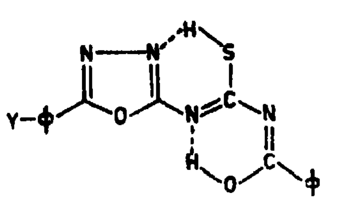


Fig. 3

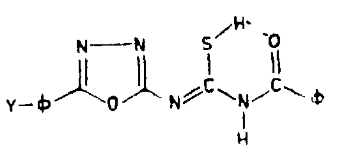


Fig. 4

The electronic spectra of the ligands show broad bands at ~250 mμ (40000 cm^{-1}) and strong broad bands at ~280 mμ (35710 cm^{-1}). These features in uv region are characteristic of longer conjugated systems, thereby causing bathochromic shift and an increase in the intensity of absorption. The ir spectra of the ligands show strong broad bands at ~3400-3200 cm^{-1} probably due to intramolecularly hydrogen bonded ν_{N-H} vibration. The overlapping of the ν_{C-H} of the phenyl group, as well as the intramolecularly hydrogen bonded ν_{O-H} with that of the ν_{N-H} is clearly indicated by the width of the band[16-17].

A weak band around the region 2600-2500 cm^{-1} is assigned to ν_{S-H} of the thiol group. Again two strong bands observed at ~1680 and 1640 cm^{-1} are assigned to $\nu_{C=O}$ in (–CO–NH) systems[17] and conjugated cyclic $\nu_{C=N}$, respectively[18-20]. The presence of a strong band at ~1180 cm^{-1} is due to the combination mode of $\nu_{NCN+C=S}$ vibrations.

TABLE 2—ELECTRONIC TRANSITIONS AND CRYSTAL FIELD PARAMETERS OF Co^{II} COMPLEXES IN cm^{-1} (EXCEPT β) AND MAGNETIC MOMENTS (μ_{eff})

Complex	$^4T_{1g}(F)\rightarrow$ $^4A_{2g}(F)(\nu_2)$	$^4T_{1g}(F)\rightarrow$ $^4T_{1g}(P)(\nu_3)$	C.T. band	μ_{eff} B.M.	D_q	B	C	F_2	F_4	β
$[Co(BPODTC)_2Cl_2]$	15150	17890	—	5.2	881.8	756.1	3503	1256.6	100.1	0.78
$[Co(BPODTC)_2Br_2]$	14930	17860	—	5.0	771.8	811.9	3758	1349.8	107.5	0.83
$[Co(BPODTC)_2(NO_3)_2]$	15040	19050	—	5.1	826.0	870	4027	1445.8	115.2	0.89
$[Co(BPODTC)_2(ClO_4)_2]$	15750	17860	—	5.3	853.1	776.4	3598	1290.4	102.8	0.80
$[Co_2(BAODTC)_2Cl_4]$	15380	18520	28570	4.2	828	828	3814	1368	108.9	0.85
$[Co_2(BAODTC)_2Br_4]$	15150	17860	27030	4.3	826	787	3446	1308	104.2	0.81
$[Co_2(BAODTC)_2(NO_3)_4]$	15380	18180	28570	4.2	841	802	3711	1382	106.0	0.82
$[Co_2(BAODTC)_2(ClO_4)_4]$	15380	17540	28570	4.1	839	763	3584	1268	100.9	0.78

TABLE 3—ELECTRONIC TRANSITIONS AND CRYSTAL FIELD PARAMETERS OF Ni^{II} COMPLEXES IN cm^{-1} (EXCEPT β) AND MAGNETIC MOMENTS (μ_{eff})

Complex	$^3A_{2g}(F)\rightarrow$ $^3T_{1g}(F)(\nu_2)$	$^3A_{2g}(F)\rightarrow$ $^3T_{1g}(P)(\nu_3)$	$^1A_{1g}\rightarrow$ $^1A_{2g}$	C.T. band	μ_{eff} B.M.	D_q	B	C	F_2	F_4	β
$[Ni(BPODTC)_2Cl_2]$	—	—	22470	27030	Dia	—	—	—	—	—	—
$[Ni(BPODTC)_2Br_2]$	—	—	22470	22400	Dia	—	—	—	—	—	—
$[Ni(BPODTC)_2(NO_3)_2]$	—	—	22470	27400	Dia	—	—	—	—	—	—
$[Ni(BPODTC)_2(ClO_4)_2]$	—	—	22470	27030	Dia	—	—	—	—	—	—
$[Ni_2(BAODTC)_2Cl_4]$	16390	27780	—	—	3.2	1054	958	4512	1603	129	0.92
$[Ni_2(BAODTC)_2Br_4]$	16180	27030	—	—	3.1	1025	932	4390	1559	125.3	0.90
$[Ni_2(BAODTC)_2(NO_3)_4]$	16130	27030	—	—	2.9	1025	932	4390	1559	165.8	0.90
$[Ni_2(BAODTC)_2(ClO_4)_4]$	16670	28570	—	—	3.0	1103	1000	4722	1674	134.0	0.96

These observations led to believe that the ligands exist in a tautomeric equilibrium. Apart from these, a number of bands also appear at ~1580, 1505, 1030 and 910 cm^{-1}. The former two bands are assigned to phenyl ring $\nu_{C=C}$ skeletal vibrations[6], whereas the later two bands are due to $\nu_{=C-O-C=}$ and ν_{N-N} vibrations of the oxadiazole ring[21-24]. The low frequency bands at ~840 and 750 cm^{-1} are assigned to aromatic *para*-disubstituted δ_{C-H} vibration and the band at 710 cm^{-1} to $\nu_{C=S}$ mode[16].

The ν_{N-H} and $\nu_{=C-O-C=}$ bands observed in the spectra of the ligands in the regions 3400-3200 and 1030 cm^{-1} remain unaffected in the spectra of the metal complexes indicating the non-coordination of the NH groups and the oxygen atom of the oxadiazole ring. But significant change is observed in the bands at ~1680, and 1180 cm^{-1}. In all the metal complexes these bands are shifted to lower frequency by 20-30 cm^{-1} suggesting the coordination of the carbonyl oxygen and thiocarbonyl sulphur atoms to the metal ion[18]. The band at ~1260 cm^{-1} (C–N) of the ligand is shifted to higher frequency region by 5-10 cm^{-1} in the spectra of the metal complexes.

The ir band at 910 cm^{-1} (N–N)[23] of the ligands (N–N) decreases in intensity and is shifted to higher frequency by 5-10 cm^{-1} in all the binuclear complexes of the type, $[M_2(BAODTC)_2X_4]$ due to π electron interaction of the oxadiazole ring of the ligand with the metal ion. This is further confirmed by bathochromic shift of the ligand band at 1640 cm^{-1} characteristic of cyclic conjugated C=N vibration due to delocalisation of the π electron over the oxadiazole moiety on complexation. This indicates that the ring nitrogen also takes part in coordination. These bands remain unaltered in the complexes of the type $[M(BPODTC)_2X_2]$ and $[M(BPODTC)_2]X_2$ suggesting non-coordination of oxadiazole ring nitrogen in these mononuclear complexes.

In the spectra of perchlorato complexes, the ir bands of the perchlorato group due to ν_{Cl-O} is split into three components appearing at 1130, 1115 and 1095 cm^{-1}. The extent of splitting indicates the presence of coordinated perchlorato group[25-26]. Coordination of the nitrate ion to the metal ion in the nitrato complexes is established by the appearance of strong additional bands at ~1390 and 1315 cm^{-1} which are the split components of ν_3 characteristic of monodentate nitrate ion[22,26]. But the absence of these bands in the nitrato and perchlorato Ni^{II} complexes with ligand BPODTC is conspicuous, indicating the counter-ions to be outside the coordination sphere.

Magnetic properties and electronic spectra : The electronic transitions, magnetic moments, *etc.* of the complexes are recorded in Tables 2-4.

TABLE 4—ELECTRONIC TRANSITIONS IN cm^{-1} AND MAGNETIC MOMENTS (μ_{eff}) FOR Cu^{II} COMPLEXES

Complex	$^2E_g\rightarrow{}^2T_{2g}$	C.T. band	μ_{eff} B.M.
$[Cu(BPODTC)_2Cl_2]$	14810	27030	1.8
$[Cu(BPODTC)_2Br_2]$	14930	27780	1.9
$[Cu(BPODTC)_2(NO_3)_2]$	14710	27400	1.9
$[Cu(BPODTC)_2(ClO_4)_2]$	14810	27030	1.7
$[Cu_2(BAODTC)_2Cl_4]$	13330	27030	0.806
$[Cu_2(BAODTC)_2Br_4]$	13790	27030	1.42
$[Cu_2(BAODTC)_2(NO_3)_4]$	14490	27400	1.65
$[Cu_2(BAODTC)_2(ClO_4)_4]$	14290	27030	1.15

TABLE 5—THERMAL STABILITY OF COMPLEXES

Complex	Temp. °C		% weight of residue
	Commencement of decomposition	Completion of decomposition	Found (Calcd.)
[Cu(BPODTC)$_2$Br$_2$]	230	580	9.85 (9.12)
[Co(BPODTC)$_2$Br$_2$]	190	580	10.82 (10.44)
[Ni(BPODTC)$_2$Cl$_2$]	160	300	9.51 (9.60)
[Cu$_2$(BAODTC)$_2$Cl$_4$]	220	700	16.88 (16.28)
[Co$_2$(BAODTC)$_2$Br$_4$]	250	880	14.42 (13.98)
[Ni$_2$(BAODTC)$_2$(ClO$_4$)$_4$]	220	400	12.58 (12.62)

The Cu^{II}, Co^{II} and Ni^{II} complexes with the ligand BAODTC are presumed to be octahedral or distorted octahedral as indicated from the band position in the electronic spectra. The sub-normal magnetic moments in these binuclear complexes are due to spin-spin interaction of the metal centres through the symmetrically bridged sulphur atom, resulting in the partial quenching of the paramagnetism. This observation further supports the view that, in case of the ligand BAODTC, the presence of a *para*-methoxy group in the phenyl ring enriches the electron density on the oxadiazole ring-nitrogen due to resonance and hence the ring nitrogen also acts as a coordinating site (Fig. 5). The Cu^{II} and Co^{II} complexes with ligand BPODTC are suggested to be octahedral in nature as indicated

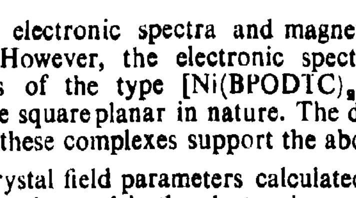


Fig. 5

M = Cu^{II}, Co^{II}, Ni^{II}.

X = Cl^-, Br^-, NO_3^-, ClO_4^-.

from the electronic spectra and magnetic moment values. However, the electronic spectra of the complexes of the type [Ni(BPODTC)$_2$]X$_2$ reveal them to be squareplanar in nature. The diamagnetic nature of these complexes support the above view.

The crystal field parameters calculated from the transitions observed in the electronic spectra of Co^{II} and Ni^{II} complexes (Tables 2 and 3) are in agreement with the earlier reports[27,28]. The β values in the octahedral complexes of Co^{II} and Ni^{II} are less than unity indicating partial covalency in the metal ligand bond.

The molar conductance values of all the complexes is low (12-20 Ω^{-1} cm^2 mol^{-1}) indicating their non-electrolytic nature except [Ni(BPODTC)$_2$]X$_2$ which is found to be ionic with λ_M values in the range 120-130 Ω^{-1} mol^{-1} cm^2.

Thermal analysis : The complexes are highly stable at room temperature and most of the complexes decompose only after 200°. No complex gives endothermic peak upto 200° which indicates the absence of either lattice water or water of crystallisation as well as the coordinated water molecules in the complexes. As seen from the thermograms, the decomposition of the complexes start around 200° indicated by exothermic peaks. On the basis of mass loss, the final residue obtained in air corresponds to the oxides of divalent metals of copper and nickel, whereas Co_3O_4 is found for the Co^{II} complexes. This is confirmed by small gain in mass in the TG curves for Co^{II} complexes at higher temperature (~600°) and is perhaps due to the oxidation of the metal from the lower valent state to the higher oxide. The endothermicity after 200° is due to the decomposition of organic ligands followed by exothermic peaks due to the oxidation of the organic products. The perchlorate complexes undergo sudden decomposition with explosion ~230° as indicated by sharp exothermic peaks in the TG curves at the same temperature. Thermal data of a few of the complexes are recorded in Table 5. A study of the decomposition pattern and the nature of the thermograms confirm to the stoichiometry suggested for the complexes.

References

1. K. C. SATPATHY, R. MISHRA and B. B. JAL, *Indian J. Chem., Sect. A*, 1983, **22**, 340
2. K. C. SATPATHY, R. MISHRA and B. B. JAL, *Indian J. Chem., Sect. A*, 1983, **22**, 613.
3. K. C. SATPATHY, R. MISHRA and B. B. JAL, *Indian J. Chem.*, in the press.
4. K. C. SATPATHY, B. B. JAL and R. MISHRA, *Tran Met. Chem.*, in the press.
5. K. C. SATPATHY, T. D. MAHANA and H. P. MISHRA, *J. Indian Chem. Soc.*, 1979, **56**, 248.
6. K. C. SATPATHY, H. P. MISHRA, A. K. PANDA, A. K. KABISATPATHY and A. TRIPATHY, *J. Indian Chem. Soc.*, 1979, **56**, 761.

7. K. C. SATPATHY and H. P. MISHRA, *Indian J. Chem., Sect. A*, 1981, **20**, 1085.
8. K. C. SATPATHY and H. P. MISHRA, *J. Indian Chem. Soc.*, 1981, **58**, 844.
9. K. C. SATPATHY, H. P. MISHRA and B. N. PATEL, *J. Indian Chem. Soc.*, 1982, **59**, 40.
10. K. C. SATPATHY, H. P. MISHRA and G. C. PRADHAN, *Indian J. Chem., Sect. A*, 1981, **20**, 612.
11. K. C. SATPATHY, H. P. MISHRA and B. N. PATEL, *Indian J. Chem., Sect. A*, 1983, **22**, 388.
12. F. L. SCOTT, T. M. LAMBA and R. N. BUTLER, *J. Chem. Soc., Perkin Trans.*, 1972, 1918.
13. R. E. LAUER and G. ZENCHEFF, *J. Heterocycl. Chem.*, 1976, **13**, 292.
14. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", 3rd. ed., E. L. B. S. and Longmans, London, 1969.
15. B. N. FIGGIS and J. LEWIS in "Modern Coordination Chemistry", eds. J. LEWIS and R. G. WILKINS, Interscience, New York, 1960, p. 415.
16. J. R. DYER, "Application of Absorption Spectroscopy to Organic Compounds", Prentice-Hall, Englewood-Cliffs, 1965, p. 34.
17. L. J. BELLAMY, "The Infrared Spectra of Complex Molecules", Methuen, London, 1966, p. 225.
18. K. C. SATPATHY, H. P. MISHRA and R. MISHRA, *J. Inorg. Nucl. Chem.*, 1981, **47**, 276.
19. B. DAS, and S. K. MAHAPATRA, *J. Inorg. Nucl. Chem.*, 1975, **37**, 27.
20. R. S. SHARMA and S. C. BAHEL, *J. Indian Chem. Soc.*, 1982, **59**, 877.
21. B. G. SAHA, R. P. BHATNAGAR and S. K. BANERJEE, *J. Indian Chem. Soc.*, 1982, **59**, 927.
22. L. J. BELLAMY, "The Infrared Spectra of Complex Molecules", Methuen, London, 1966, p. 350.
23. N. B. SINGH and J. SINGH, *J. Inorg. Nucl. Chem.*, 1978, **40**, 919.
24. I. K. VERMA and C. K. GEETHA, *Indian J. Chem., Sect. A*, 1978, **16**, 352.
25. B. J. HATHWAY and A. E. UNDERHILL, *J. Chem. Soc.*, 1961, 3091.
26. N. SAHA and K. M. DATTA, *J. Indian Chem. Soc.*, 1982, **59**, 728.
27. A. B. P. LEVER, "Inorganic Electronic Spectroscopy", Elsevier, London, 1968, p. 355.
28. C. J. BALLHAUSEN, "Introduction to Ligand Field Theory", McGraw-Hill, New York, 1962, p. 245.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 951-955

Organophosphonic Acids as Complexones. Part-VII. Divalent Metal Derivatives of 1-Aminoethylidenediphosphonic Acid and 1-Aminobenzylidenediphosphonic Acid

B. VENKATESWARA RAO, NEELAM PALTA, S. N. DUBEY and D. M. PURI*

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

Reactions of 1-aminoalkylidene-/arylidenediphosphonic acids with bivalent metal salts, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Pb^{II} yielded solid products of general formula $M_2L.xH_2O$, in which metal is hexa-coordinated as has been inferred from their electronic spectra. Coordination sites have been established from infrared studies. Subnormal magnetic moment values and other physical properties suggest them to be polymeric in nature.

COMPLEX forming properties of 1-hydroxyethylidenediphosphonic acid (HEDP) have been reported earlier from these laboratories[1,2]. 1-Aminoalkylidenediphosphonic acids are structurally similar ligands. The basic centre $-OH$ in 1-hydroxyalkylidenediphosphonic acids has been replaced by $-NH_2$ group in this type of ligands. These ligands have been reported to have herbicidal and fungicidal properties[3]. Therefore, with the view that metal ions might enhance these properties, in the present work attempt has been made to explore complexing potentialities of these ligands by isolating their metal derivatives from aqueous medium.

Experimental

1-Aminoethylidenediphosphonic acid (AEDP) was prepared by the reaction of acetanilide with phosphorus trichloride and diethylphosphite in 1 : 3 : 1 molar ratio[4]. 1-Aminobenzylidenediphosphonic acid (ABDP) has, however, been prepared by the reported method[5].

Preparation of metal derivatives : Bivalent metal salts (B.D.H.) were used as such.

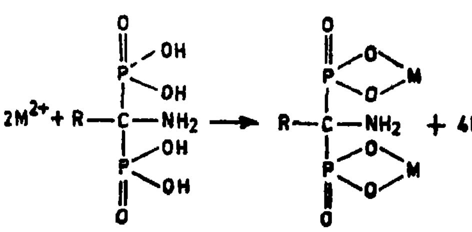
The metal derivatives of both AEDP and ABDP were prepared by mixing 0.002 mole of aqueous solution of metal salt with 0.001 mole of the ligand solution with constant stirring. In case of AEDP, it was followed by the dropwise addition of a solution 0.004 mole of NaOH. However, with ABDP, complex precipitation was possible even on direct mixing and there was no need for neutralisation of the liberated hydrogen ions. Addition of acetone/methanol to the reaction mixture helped in improving the yield of the product. The precipitates were washed with 50% acetone to free the product from starting metal salt and then dried at 60-70°. The analytical data showed the complexes as having general formula $M_2L.xH_2O$, where L = AEDP or ABDP, and x = 1-3.

Reactions in the 1 : 1 molar ratio of metal and ligand also resulted in the formation of M_2L complexes and no complexes with partial replacement of acidic hydrogens could be isolated.

Infrared spectra in the form of KBr pellets were recorded on Beckman IR-20 spectrophotometer. Mull spectra in the 200-2000 nm region were run on DMR-21 spectrophotometer. Magnetic measurements at room temperature were made on PAR 155 vibrating sample magnetometer. Thermal analyses of some of the compounds were done at N.C.L., Pune in the atmosphere of air and in platinum crucible, using alumina as the standard.

Results and Discussion

Reaction between bivalent metal salt and 1-aminoethylidenediphosphonic acid (AEDP) or 1-aminobenzylidenediphosphonic acid (ABDP) in the molar ratio of 2 : 1 yielded compounds with general formula $M_2L.xH_2O$, where x may have the value from 1 to 3 which were inferred from elemental analyses (Table 1). The compounds once precipitated did not dissolve in water or any other common organic solvent. The metal derivatives did not melt even up to 270°. The reactions can be represented by the following equation.



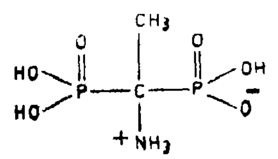
The structures of the complexes were determined by infrared and electronic spectral, and magnetic measurement studies.

The infrared spectrum of 1-aminoethylidenediphosphonic acid suggested that the ligand exists

TABLE 1—ANALYTICAL AND MAGNETIC MOMENT DATA OF METAL DERIVATIVES OF AEDP AND ABDP

Complex	Colour	Analysis % : Found/(Calcd.)		μ_{eff}
		M	P	B.M.
$Mn_2(C_2H_5O_6NP_2).2H_2O$	White	31.02 (31.68)	17.15 (17.87)	4.12
$Co_2(C_2H_5O_6NP_2).3H_2O$	Blue violet	30.59 (31.62)	16.25 (16.63)	3.48
$Ni_2(C_2H_5O_6NP_2).4H_2O$	Light green	30.58 (30.07)	15.25 (15.88)	2.31
$Cu_2(C_2H_5O_6NP_2).2H_2O$	Light blue	33.13 (34.90)	16.75 (17.03)	1.89
$Zn_2(C_2H_5O_6NP_2).3H_2O$	White	32.89 (33.90)	15.86 (16.07)	—
$Cd_2(C_2H_5O_6NP_2).2H_2O$	White	49.01 (48.68)	13.21 (13.48)	—
$Pb_2(C_2H_5O_6NP_2).H_2O$	White	63.02 (65.43)	9.65 (9.79)	—
$Mn_2(C_7H_7O_6NP_2).H_2O$	White	29.65 (30.16)	15.41 (15.86)	4.04
$Co_2(C_7H_7O_6NP_2).2H_2O$	Violet	28.71 (28.28)	15.12 (14.87)	3.85
$Ni_2(C_7H_7O_6NP_2).2H_2O$	Light green	28.64 (28.19)	15.85 (14.89)	2.5
$Cu_2(C_7H_7O_6NP_2).H_2O$	Light blue	31.52 (31.14)	15.49 (15.19)	1.82
$Zn_2(C_7H_7O_6NP_2).H_2O$	White	32.28 (31.76)	15.32 (15.06)	—
$Cd_2(C_7H_7O_6NP_2).H_2O$	White	44.96 (44.43)	12.48 (12.26)	—
$Pb_2(C_7H_7O_6NP_2).H_2O$	White	60.53 (59.60)	9.25 (8.97)	—

as a zwitterion. The two bands at 1160 and 1020 cm^{-1} correspond to ν_{asPO_2} and ν_{sPO_2} vibrations in HPO_2 group. In addition, ν_{asP-OH} and ν_{sP-OH} bands corresponding to $P(OH)_2$ also appeared at 1000 and 940 cm^{-1}. Bands at 3160-2960 and 1500 cm^{-1} have been assigned to stretching and bending mode of $\overset{+}{N}H_3$. Phosphoryl frequency was observed at 1200 cm^{-1}.



Infrared spectrum of 1-aminobenzylidenediphosphonic acid showed only two bands at 1010 and 930 cm^{-1} in the region of phosphonic group which could be assigned to asymmetric and symmetric stretching vibrations of $P(OH)_2$ group. Phosphoryl stretching frequency, $\nu_{P=O}$, appeared at 1230 cm^{-1}. The stretching and bending mode of NH_2 group have been observed at 3400 cm^{-1} and 1580 cm^{-1}, respectively.

The frequencies of the principal bands in the ir spectra of AEDP and its metal derivatives have been given in Table 2. Stretching vibrations of phosphoryl group in case of metal derivatives have been observed at 1110-1155 cm^{-1}. The displacement of the band by 50-100 cm^{-1} towards lower frequency has been attributed to the formation of coordination bond between phosphoryl oxygen and metal ion. Such observations have also been made in case of polyaminopolyphosphonic acids reported from these laboratories[6,7] and are also in agreement with the observations of Khramov *et al.*[8] for compounds of 1-hydroxyethylidenediphosphonic acid. The asymmetric and symmetric mode of stretching vibration of PO_3 group appeared at 1070-1020 and 1000-900 cm^{-1} ranges, respectively and splitting of these bands was observed. Such splitting is expected in view of the partial covalent character of M – O bond due to lowering of the symmetry of PO_3 group.

Similar to AEDP complexes, lowering in $\nu_{P=O}$ has also been observed in metal derivatives of ABDP (Table 3) and absorptions due to asymmetric and symmetric modes of PO_3 group appeared at 1040 ± 10 and 980-990 cm^{-1}, respectively.

Participation of NH_2 group in coordination to metal ion could not be inferred from the ir spectra due to C – N bands being very weak and masking of N – H bands by broad O – H bands.

Electronic spectra and magnetic measurements : Due to the insolubility of the complexes in common solvents, it was not possible to study their solution spectra. Therefore, mull spectra in 200-2000 nm region has been studied. The metal derivatives of ABDP also absorbed in the same regions as those of AEDP. Therefore, only the spectra of AEDP complexes has been discussed in detail.

Manganese(II) complexes : Manganese(II) formed a light pink complex, $Mn_2(AEDP).2H_2O$ with

TABLE 2—PRINCIPAL BANDS (cm^{-1}) IN INFRARED SPECTRA OF AEDP AND ITS METAL DERIVATIVES

AEDP	$Mn_2L.2H_2O$	$Co_2L.3H_2O$	$Ni_2L.4H_2O$	$Cu_2L.2H_2O$	$Zn_2L.3H_2O$	$Cd_2L.2H_2O$	$Pb_2L.H_2O$	Assignment
3400 3160	3320 3210	3340 3260	3440 3340	3300 br	3360 3260	3400 br	3460 3400	ν_{+OH}
2960		3120	3200		3200			ν_{NH_3}/ν_{NH_2}
		1650	1620	1625	1620	1620	1620	$\delta_{O-H}, \delta_{N-H}$
1630 1200	1625 1110	1620 1120	1560 1120	1155 1110	1140	1120 1110		$\nu_{P=O}$
1130	—	—	—	—	—	—	—	ν_{asPO_3}
	1080 1050 1020	1050 1030 1015	1070 1050 1020	1090 1070 1030	1080 1050	1050 1020	1080 1040	ν_{asPO_3}
1020	—	—	—	—	—	—	—	ν_{sPO_3}
1000	—	—	—	—	—	—	—	$\nu_{asP-(OH)_2}$
	990	990	950	1000	1000	960	980	ν_{sPO_3}
	910	910	900	920	940	910		
940	—	—	—	—	—	—	—	$\nu_{sP-(OH)_2}$

br = Broad.

TABLE 3—PRINCIPAL BANDS (cm^{-1}) IN INFRARED SPECTRA OF ABDP AND ITS METAL DERIVATIVES

ABDP	$Mn_2L.H_2O$	$Co_2L.2H_2O$	$Ni_2L.2H_2O$	$Cu_2L.H_2O$	$Zn_2L.H_2O$	$Cd_2L.H_2O$	$Pb_2L.H_2O$	Assignments
3400 br	3000 br	3260 br	3300 br	3200 br	3340	3360 br	3400	ν_{OH}, ν_{NH_2}
1640	1640 1630	1630	1650 1640	1650 1620	1630	1640	1620	$\delta_{O-H}, \delta_{N-H}$
1230	1190	1150	1140	1190	1180	1105	1180	$\nu_{P=O}$
	1060 1080	1030	1160	1050	1040	1050	1040	ν_{asPO_3}
1010	—	—	—	—	—	—	—	$\nu_{asP-(OH)_2}$
—	980	900	980	990	1000	990	960	ν_{sPO_3}
930	—	—	—	—	—	—	—	$\nu_{sP-(OH)_2}$

br = Broad.

AEDP. It absorbed at 25970, 8330 and 6900 cm^{-1} in the electronic spectrum. But it is not possible to assign any geometry to the complex on this basis, since diffused transmittance spectra does not give any information about the oscillator strength. $Mn_2(ABDP).H_2O$ is a white solid and hence did not absorb in this region.

The magnetic moment values of 4.12 B.M. for AEDP complex and 4.04 B.M. for ABDP complex are somewhat lower than the expected value, 5.65-6.10 B.M., for d^5 system[9]. This shows that the system is magnetically concentrated. The metal ions are situated close enough so that there is considerable interaction between them.

Cobalt(II) complexes : The two blue-violet complexes showed electronic spectrum typical of six-coordinate complexes. The absorption bands have been observed at 8160, 16390, 17540 and 20000 cm^{-1} for $Co_2(AEDP).3H_2O$ and at 8260 (weak), 18020 and 19800 cm^{-1} for $Co_2(ABDP).2H_2O$, and the assignments mode for these bands are to the excited state terms $^4T_{2g}(F)$, $^4A_{2g}(F)$ and $^4T_{1g}(P)$, respectively from the ground term $^4T_{1g}(F)$. The frequency on visible band at 16390 cm^{-1} can arise through low symmetry components to the ligand field or through the presence of spin-forbidden transition made evident by intensity stealing from the allowed band[10]. The presence of low symmetry components to the ligand field is revealed by the splitting[11] of near infrared band 7170, and 8160 cm^{-1}.

The magnetic moment values have been found to be 3.43 and 3.85 B.M. corresponding to $Co_2(AEDP).3H_2O$ and $Co_2(ABDP).2H_2O$, which indicate that antiferromagnetic interactions are operative.

Nickel(II) complexes : Both the nickel(II) complexes are light green in colour which may be due to the presence of bands in the red and blue portions of the visible spectrum. The three bands at 8440, 14290 and 25000 cm^{-1} for $Ni_2(AEDP).H_2O$, and 8300, 13890 and 25640 cm^{-1} for $Ni_2(ABDP).2H_2O$ are associated with spin-allowed transitions from the $^3A_{2g}(F)$ ground term to the three excited triplet terms $^3T_{2g}(F)$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$, respectively. In case of $Ni_2(ABDP).2H_2O$ complex there are also

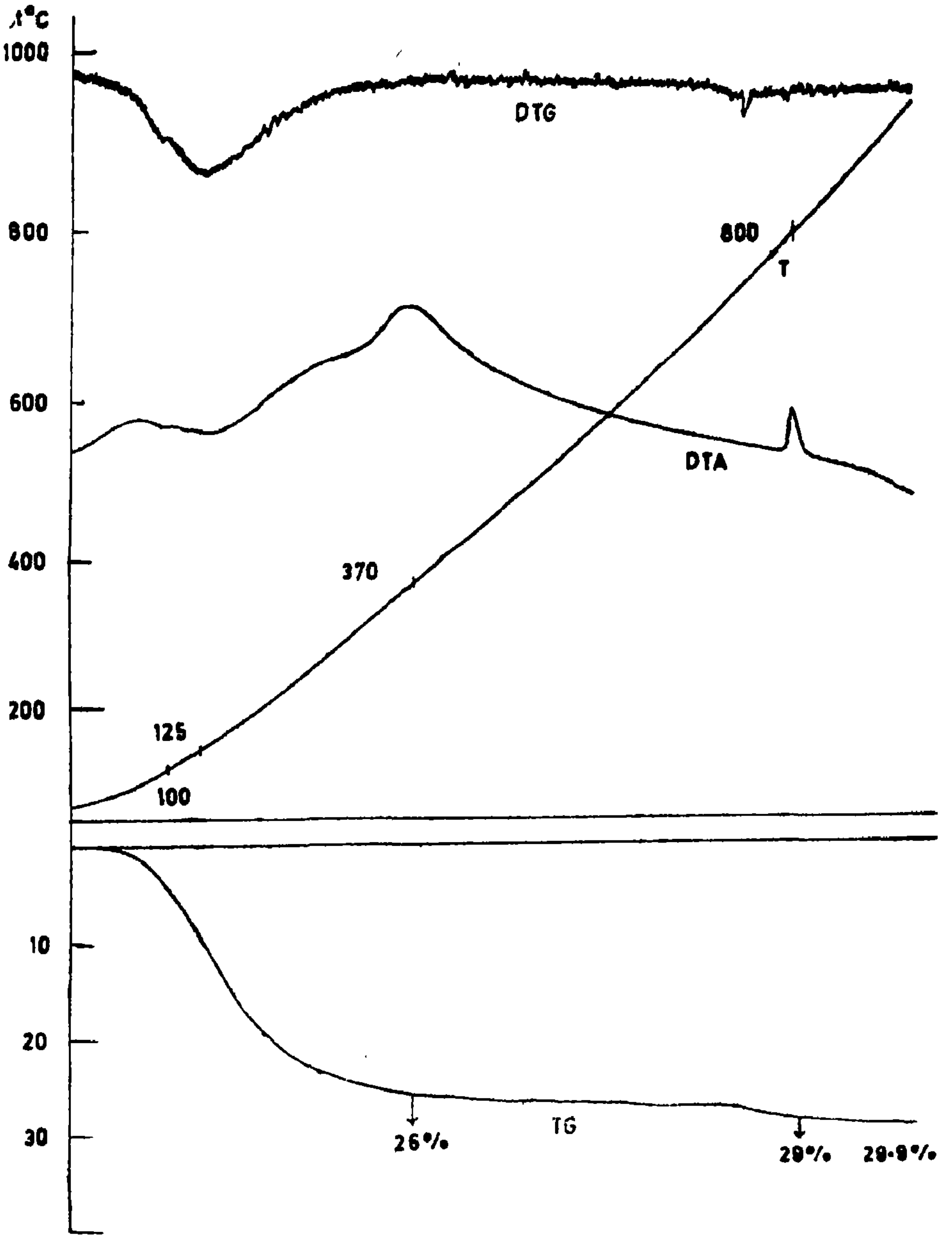


Fig. 1. Derivatogram of $Ni_2(C_7H_8NO_6P_2).2H_2O$ (100 mg specimen).

weak bands at ($f \sim 10^{-6}$) in the region of 15000-18000 cm^{-1} (at 15630 and 17390 cm^{-1}) may be attributed to spin-forbidden transitions[18]. The three spin-allowed transitions suggest the formation of an octahedral six-coordinate nickel(II) complex. The spin-forbidden transition could be interpretted in terms of spin-orbit coupling.

The magnetic moment for Ni^{II} octahedral in dilute systems are normally found to vary from 2.80 to 3.50 B.M. However, in the $Ni_2(AEDP).4H_2O$ and $Ni_2(ABDP).2H_2O$ complexes, magnetic moments have been observed to be 2.31 and 2.50 B.M., respectively. Therefore, like other metal derivatives, these complexes have also been inferred to be magnetically concentrated.

Copper(II) complexes : $Cu_2(AEDP).2H_2O$ gave a single broad band in the visible region at 13160 cm^{-1} and has been attributed to $^2T_{2g} \leftarrow {}^2E_g$ transition in six-coordinated geometry.

The magnetic moment values of 1.45 and 1.32 B.M. for AEDP and ABDP complexes, respectively are lower than the expected value of 1.7-2.20 B.M. range for d^9 system.

Thermal analyses :

Nickel(II)aminobenzylidenediphosphonate : The endothermic effects at 100 and 125 on the D.T.A. curve for $Ni_2(ABDP).2H_2O$ (Fig. 1) correspond to the consecutive loss of first and second water molecules, respectively. Two exothermic effects at 370

and 800° are observed. On D.T.A. curve, the corresponding mass loss on T.G. is 26 and 29%, respectively. However, no definite stages of decomposition could be identified after the total loss of water molecules from the complex compound suggesting that the organic part starts decomposing after the total loss of water molecules. The final product is $2NiO.P_2O_5$ as inferred from total experimental mass loss of 29.9% (theoretical 30%) of the complex. The formation of the final product of this type has also been reported by Khramov *et al.*[8] for their rare earth organophosphonic acid complexes.

In case of $Co_2(AEDP).3H_2O$ the endothermic effect at 140° on D.T.A. curve corresponds to the loss of three molecules of water. The total experimental mass loss of 23% at the formation of $2NiO.P_2O_5$ is corroborated by the expected loss of 21.73%.

The properties of these complexes like insolubility in different solvents, their infusibility up to 280°, coordination of phosphoryl oxygen of the ligands to the metal atom and other physico-chemical studies suggest that these may be polymeric in nature.

Acknowledgement

Thanks are due to the Chairman, Department of Chemistry for facilities and one of the authors (B.V.R.) is thankful to I.N.S.A., New Delhi for financial assistance.

References

1. D. M. PURI and N. PALTA, *Indian J. Chem.*, 1982, **21**, 624.
2. D. M. PURI, B. V. RAO, N. PALTA and S. N. DUBEY, *J. Indian Chem. Soc.*, in the press.
3. B. R. J. DELVIN, *Chem. Abstr.*, 1979, **90**, 34889; W. HOYLE and R. VOGEL, *Chem. Abstr.*, 1980, **93**, 181016.
4. W. PLOGER, N. SCHINDLER, K. WOLLMANN and K. N. WORMS, *Z. Anorg. Allg. Chem.*, 1972, **389**, 119.
5. I. LERCH and A. KOTTLER, Ger. Pat., 1002355/1957 (*Chem. Abstr.*, 1959, **53**, 21814).
6. N. PALTA, B. V. RAO, S. N. DUBEY and D. M. PURI, *Polyhedron*, 1984, **3**, 527.
7. N. PALTA, B. V. RAO, S. N. DUBEY and D. M. PURI, *Indian J. Chem., Sect. A*, 1984, **23**, 397.
8. V. P. KHRAMOV and A. A. KOL'TSOV, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1973, **18**, 1567.
9. J. LEWIS and R. G. WILKINS, "Modern Coordination Chemistry", Interscience, New York, 1967.
10. D. NICHOLLS, "Pergamon Texts in Inorganic Chemistry", Pergamon, New York, 1975, p. 24.
11. A. B. P. LEVER, *Inorg. Chem.*, 1965, **4**, 1042.
12. A. B. P. LEVER, "Inorganic Electronic Spectronic Spectroscopy", Elsevier, Amsterdam, 1968, p. 333.

J. Indian Chem. Soc.,
Vol. LXI, November, December, 1984, pp. 956-959

Dissociation Constants of Acetic Acid in Methanol-Water Media at Different Temperatures and Related Thermodynamic Quantities

D. C. BHATTACHARYYA, A. K. BASU** and S. ADITYA*

Department of Chemical Technology, University of Calcutta, Calcutta-700 009

Dissociation constants of acetic acid in methanol-water media containing 30, 45, 60, 75 and 90% by weight of methanol at 15, 20, 25, 30 and 35° have been determined using the cell

Pt, H_2(g) | HOAc(M_1), NaOAc(m_2), NaCl(m_3) methanol (X), water (100 – X) | AgCl, Ag.

At any temperature, the pK_a increases as the solvent becomes enriched in methanol. In media with any particular composition, pK_a over the temperature range passes through a minimum. ΔG°, ΔH°, ΔS° and ΔC°_p for the dissociation process at 25° have been calculated.

IN our programme[1-8] to determine the standard potentials of Hg, Hg_2-X_2/X^-, where X^- is acetate or propionate ion, for the standard potentials of mercury/mercurous acetate electrode in dioxane-water, and mercury/mercurous propionate electrodes in water and dioxane-water media, we used the values of the dissociation constants of acetic acid and propionic acid in the respective media as reported by Harned and coworkers[4-8]. While extending the determination in methanol-water media we found that the dissociation constants over a wide range of solvent-composition and temperature are not available in the literature. Harned and Embree[9] determined the values of K_a only in 10 and 20% of methanol at different temperatures. Bacarella *et al.*[10] determined the *p*K values in methanol-water media at 25° using glass electrode and Shedlovsky and Kay[11] by conductometric method. Recently, Paabo, Robinson and Bates[12] determined the values of *p*K over a temperature range of 10-40° but only in 50% methanol. In this communication we report the dissociation constants of acetic acid in 30, 45, 60, 75 and 90% by weight of methanol and at 15, 20, 25, 30 and 35°.

Experimental

Methanol (A.R., B.D.H.) was refluxed with iodine and sodium hydroxide and then distilled. The distillate was further refluxed with Zn-dust and KOH and subsequently distilled. The middle fraction was collected for use. The methods for the purification of acetic acid, the preparation of hydrogen electrode and the cell set-up have been described in our previous communication[1].

The silver-silver chloride electrodes used are of thermal electrolytic type and have been prepared by the method recommended by Bates[13]. Cells of the type similar to that used by Harned and Ehlers[15],

Pt, H_2(g) | HOAc(m_1), NaOAc(m_2), NaCl(m_3) methanol (X), water (100 – X) | AgCl, Ag,

have been used in the present measurements. We have used buffered solutions in the cell since the errors[16-19] that vitiate the dissociation constants of polybasic acids from the use of buffered solutions because of ion association of poly-valent anions, does not arise in the case of acetic acid. The measurements have been taken at five temperatures, 15, 20, 25, 30 and 35° with a Leeds-Northrup K_2 potentiometer and galvanometer, the cell e.m.f. values being measured first from 25 to 35° and then from 15 to 25°. The measured e.m.f. readings have been corrected to that for the standard 1 atmosphere pressure of hydrogen using the expression[14],

$$\Delta E = 2.3026 \frac{RT}{2F} \log \frac{760}{(P-P_s)},$$

where P = barometric pressure, and P_s = vapour pressure of the solvent.

The vapour pressures of methanol-water systems at different temperatures and of different compositions have been taken from the work of Harned and coworkers[20] and Melton and Amis[21]. The corrected e.m.f. values for the cell presented in Table 1 are the average of four sets. The e.m.f. values at 25° at the first and at the last readings were in good agreement (always <0.05 mV) and their values are the average of eight readings.

** Department of Chemistry, Midnapore College, Midnapore.

TABLE 1—E.m.f. VALUES OF CELL (E/V) CORRECTED TO 1 Atm PRESSURE OF H_2 AT DIFFERENT TEMPERATURES

Pt, H_2(g) | HOAc(m_1), NaOAc(m_2), NaCl(m_3) methanol (X%), water (100 − X) % | AgCl, Ag

m_1	$m_2 = m_3$	Temperature °C				
		15	20	25	30	35
		30% Methanol				
0.5189	0.0915	0.52022	0.52344	0.52655	0.52930	0.53201
0.4985	0.0879	0.52141	0.52459	0.52767	0.53041	0.53311
0.4679	0.0826	0.52382	0.52646	0.52950	0.53224	0.53493
0.4371	0.0771	0.52528	0.52834	0.53135	0.53406	0.53675
0.4065	0.0717	0.52731	0.53039	0.53336	0.53607	0.53875
0.3937	0.0436	0.52949	0.53231	0.53496	0.53748	0.53996
0.3518	0.0390	0.53245	0.53528	0.53792	0.54046	0.54295
0.2678	0.0297	0.53976	0.54259	0.54524	0.54783	0.55037
0.2471	0.0274	0.54187	0.54471	0.54737	0.54997	0.55254
0.2263	0.0251	0.54418	0.54703	0.54970	0.55232	0.55491
		45% Methanol				
0.5554	0.0615	0.52962	0.53234	0.53502	0.53741	0.53958
0.4801	0.0532	0.53407	0.53678	0.53936	0.54177	0.54395
0.3964	0.0439	0.53979	0.54241	0.54501	0.54743	0.54964
0.3546	0.0393	0.54298	0.54556	0.54816	0.55060	0.55283
0.3128	0.0347	0.54662	0.54919	0.55178	0.55425	0.55650
0.1225	0.0309	0.57027	0.57320	0.57614	0.57900	0.58162
0.1106	0.0288	0.57298	0.57592	0.57887	0.58176	0.58442
0.0989	0.0249	0.57622	0.57915	0.58211	0.58502	0.58770
0.0750	0.0189	0.58369	0.58665	0.58965	0.59265	0.59541
0.0632	0.0159	0.58839	0.59138	0.59442	0.59747	0.60030
		60% Methanol				
0.3309	0.0957	0.54486	0.54778	0.55078	0.55366	0.55678
0.3095	0.0895	0.54735	0.55020	0.55315	0.55601	0.55909
0.2839	0.0821	0.55049	0.55326	0.55615	0.55900	0.56202
0.2582	0.0747	0.55378	0.55647	0.55931	0.56215	0.56512
0.2326	0.0673	0.55742	0.56004	0.56283	0.56566	0.56859
0.2072	0.0599	0.56128	0.56382	0.56658	0.56941	0.57229
0.1816	0.0525	0.56555	0.56803	0.57076	0.57359	0.57644
0.1562	0.0452	0.57038	0.57282	0.57551	0.57836	0.58119
0.1044	0.0302	0.58226	0.58463	0.58731	0.59023	0.59304
0.0789	0.0228	0.59021	0.59258	0.59529	0.59828	0.60112
		75% Methanol				
0.2095	0.0606	0.56393	0.56660	0.57013	0.57276	0.57541
0.1772	0.0571	0.56889	0.57162	0.57501	0.57767	0.58036
0.1656	0.0534	0.57144	0.57401	0.57740	0.58004	0.58274
0.1481	0.5478	0.57558	0.57803	0.58128	0.58390	0.58662
0.1364	0.0440	0.57846	0.58083	0.58399	0.58661	0.58933
0.1188	0.0383	0.58321	0.58547	0.58849	0.59109	0.59384
0.1014	0.0327	0.58843	0.59059	0.59350	0.59610	0.59888
0.0898	0.0290	0.59226	0.59436	0.59719	0.59981	0.60261
0.0782	0.0252	0.59665	0.59871	0.60147	0.60410	0.60694
0.0668	0.0216	0.60137	0.60339	0.60610	0.60876	0.61164
		90% Methanol				
0.0732	0.0236	0.60245	0.60541	0.60907	0.61236	0.61602
0.0684	0.0221	0.60462	0.60748	0.61104	0.61429	0.61790
0.0661	0.0213	0.60594	0.60875	0.61226	0.61548	0.61908
0.0589	0.0190	0.60973	0.61240	0.61577	0.61895	0.62247
0.0481	0.0155	0.61620	0.61866	0.62181	0.62494	0.62837
0.0408	0.0132	0.62123	0.62357	0.62660	0.62970	0.63308
0.0344	0.0111	0.62640	0.62864	0.63157	0.63466	0.63800
0.0252	0.0081	0.63529	0.63740	0.64021	0.64330	0.64663
0.0194	0.0063	0.64248	0.64456	0.64732	0.65046	0.65380
0.0134	0.0043	0.65252	0.65458	0.65734	0.66055	0.66395

TABLE 2—VALUES OF $-\log K'_A$ AT DIFFERENT TEMPERATURES

Ionic strength	Temperature, °C				
	15	20	25	30	35
	30% Methanol				
0.1880	5.1655	5.1738	5.1843	5.1942	5.2066
0.1758	5.1689	5.1762	5.1859	5.1954	5.2073
0.1652	5.1748	5.1808	5.1894	5.1982	5.2095
0.1542	5.1786	5.1836	5.1910	5.1990	5.2096
0.1434	5.1834	5.1872	5.1935	5.2008	5.2108
0.0872	5.2076	5.2063	5.2066	5.2108	5.2167
0.0780	5.2106	5.2085	5.2078	5.2109	5.2167
0.0594	5.2201	5.2158	5.2131	5.2150	5.2197
0.0548	5.2220	5.2174	5.2142	5.2158	5.2202
0.0502	5.2241	5.2189	5.2153	5.2165	5.2207
	45% Methanol				
0.1230	5.5118	5.5221	5.5329	5.5413	5.5508
0.1064	5.5267	5.5346	5.5434	5.5508	5.5593
0.0878	5.5433	5.5487	5.5553	5.5615	5.5689
0.0786	5.5506	5.5546	5.5601	5.5658	5.5726
0.0694	5.5598	5.5626	5.5669	5.5721	5.5788
0.0618	5.5666	5.5683	5.5718	5.5765	5.5822
0.0576	5.5694	5.5705	5.5734	5.5779	5.5834
0.0498	5.5774	5.5774	5.5794	5.5834	5.5884
0.0378	5.5881	5.5864	5.5870	5.5903	5.5946
0.0318	5.5955	5.5930	5.5928	5.5957	5.5997
	60% Methanol				
0.1914	5.6940	5.7211	5.7444	5.7644	5.7981
0.1790	5.7085	5.7337	5.7554	5.7745	5.8069
0.1642	5.7259	5.7478	5.7686	5.7866	5.8178
0.1494	5.7422	5.7627	5.7808	5.7977	5.8267
0.1346	5.7605	5.7787	5.7950	5.8108	5.8382
0.1198	5.7778	5.7936	5.8082	5.8230	5.8486
0.1050	5.7951	5.8086	5.8214	5.8351	5.8590
0.0904	5.8142	5.8254	5.8364	5.8490	5.8718
0.0604	5.8473	5.8538	5.8612	5.8716	5.8904
0.0456	5.8646	5.8688	5.8743	5.8837	5.9009
	75% Methanol				
0.1212	6.1451	6.1801	6.2220	6.2489	6.2750
0.1142	6.1590	6.1919	6.2316	6.2577	6.2832
0.1068	6.1744	6.2053	6.2427	6.2678	6.2928
0.0956	6.1982	6.2258	6.2597	6.2885	6.3077
0.0880	6.2129	6.2384	6.2699	6.2928	6.3164
0.0760	6.2360	6.2581	6.2860	6.3074	6.3302
0.0654	6.2588	6.2776	6.3021	6.3221	6.3440
0.0580	6.2728	6.2896	6.3117	6.3309	6.3522
0.0504	6.2898	6.3039	6.3236	6.3418	6.3626
0.0432	6.3040	6.3165	6.3340	6.3513	6.3715
	90% Methanol				
0.0472	7.0557	7.0928	7.1368	7.1737	7.2219
0.0442	7.0645	7.0992	7.1409	7.1767	7.2235
0.0426	7.0722	7.1057	7.1462	7.1812	7.2274
0.0380	7.0887	7.1186	7.1556	7.1890	7.2330
0.0310	7.1138	7.1382	7.1698	7.2006	7.2415
0.0264	7.1303	7.1511	7.1792	7.2082	7.2470
0.0222	7.1474	7.1648	7.1898	7.2172	7.2541
0.0162	7.1669	7.1796	7.2000	7.2251	7.2594
0.0126	7.1798	7.1897	7.2073	7.2311	7.2687
0.0086	7.1942	7.2009	7.2155	7.2377	7.2686

Results and Discussion

The e.m.f. of the cell (1) is related to the concentration of hydrogen ion, m_H, and that of chloride ion, m_{Cl}, by the equation (1).

$$E = E^\circ - \frac{RT}{F} \ln m_H\, m_{Cl}\, \gamma_H\, \gamma_{Cl} \qquad (1)$$

where E° is the standard potential of Ag, AgCl electrode and γ_H and γ_{Cl} are the activity coefficients of hydrogen and chloride ions, respectively. The standard potential of silver, silver chloride electrode has been taken from the work of Harned and coworkers[20] and Austin *et al.*[22]. In the equation (1), $m_H\, \gamma_H$ may be eliminated by introducing the expression for the dissociation constant of acetic acid

which is expressed as in equation (2).

$$K_a = \frac{m_H\, m_{OAc}}{m_{HOAc}} \frac{\gamma_H\, \gamma_{OAc}}{\gamma_{HOAc}} \qquad (2)$$

$$[HOAc \rightleftharpoons H + OAc]$$

The equation then reduces to equation (3).

$$\frac{(E-E^{\circ})F}{2.3026\,RT} + \log \frac{m_{Cl} m_{HOAc}}{m_{OAc}} = -\log k_a - \log \frac{\gamma_{Cl} \gamma_{HOAc}}{\gamma_{OAc}} \qquad (3)$$

Now, the molalities of the ionic and unionised are given as,

$m_{Cl} = m_s$ = molality of NaCl,

$m_{HOAc} = m_1 - m_H$,

and $m_{OAc} = m_s + m_H$ (m_s = molality of sodium acetate).

With the assumptions, (i) m_H, the molality of hydrogen ion from the dissociation of acetic acid being of the order of $K_a(m^1/m_s)$ is negligible as compared to m_s and m_1, and (ii) the activity of the two uni-valent ions, namely γ_{OAc} and γ_{Cl}, are the same and as such cancel each in the equation (3), the equation (3) may be written in the form

$$\frac{(E-E^{\circ})F}{2.3026\,RT} + \log \frac{m_1 m_s}{m_s} = \log K_a - \log \gamma_{HOAc}. \qquad (4)$$

Long and McDevit[23] have discussed that for buffer solutions the effect of salt on the activity coefficient of acetic acid or any molecular species can be represented by equation (5).

$$\log \gamma_{HOAc} = SI \qquad (5)$$

where I is the ionic strength of the solution and S is kown as salting coefficient.

Thus, we have

$$\frac{(E-E^{\circ})F}{2.3026\,RT} + \log \frac{m_1 m_s}{m_s} = -\log K_a = SI \qquad (6)$$

The left hand side of equation (6) is denoted by $\log K'_a$. From the equation. it is apparent that the plot of $\log K'_a$ against the ionic strength, I, is linear and the intercept at the zero ionic strength gives $\log K_a$ and hence K_a, the thermodynamic dissociation constant.

The values of pK_a in methanol-water media of different ionic strengths (column 3) at 15, 20, 25, 30 and 35° are given in columns 4, 5, 6, 7 and 8, respectively. Column 3 of Table 3 presents the thermodynamic dissociation constant (pK_a).

The values of pK_a have been fitted to the equation[24]

$$pK_a = A^*/T - D^* + C^*T \qquad (7)$$

where T is the Kelvin temperature using the method of least squares.

With $\log K_a$ expressed in the form of equation (7) we have the thermodynamic quantities, ΔG°, the Gibbs' free energy change, ΔH°, the enthalpy change, ΔS°, the entropy change, and ΔC_p°, the heat capacity change for the dissociation process by standard procedure in the following forms.

$$\Delta G^{\circ} = 2.303\ RT\ pK_a$$

$$\Delta H^{\circ} = 2.3026\ RA^* - 2.3026\ KC^*\ T^2$$

$$\Delta C_p^{\circ} = -2 \times 2.3026\ RC^*\ T$$

and $$\Delta S^{\circ} = 2.3026\ RD^* - \Delta C_p^{\circ}.$$

Columns 4, 5, 6 and 7 present the ΔG°, ΔS°, ΔH° and ΔC_p°, respectively for the ionisation process at 25°. The quantities for 20, 30 and 50% methanol from literature have also been incorporated (Table 3).

TABLE 3—pK_a VALUES AND RELATED THERMODYNAMIC QUANTITIES FOR DISSOCIATION OF ACETIC ACID IN METHANOL-WATER MEDIA AT DIFFERENT TEMPERATURES

Solvent % Methanol	Temp. °C	pK_a	ΔG° cal mol^{-1}	ΔS° cal mol^{-1} deg^{-1}	ΔH° cal mol^{-1}	ΔC_p° cal mol^{-1}
0	25	4.772	6486	−22.1	−92	−36.5[a]
		4.774	6488	−22.1	−95	−37[b]
10	25	4.928	6690	−22.3	30	−43.3[a]
20	25	5.098	6929	−22.7	108	−47.1[a]
30	15	5.246				
	20	5.286				
	25	5.227	7130	−22.5	407.9	−52.2
	30	5.225				
	35	5.226				
45	15	5.622				
	20	5.615				
	25	5.611	7654	−25.0	144.0	−54.7
	30	5.612				
	35	5.614				
50	25	5.6600	7721	−26.2	−52	−54[b]
60	15	5.918				
	20	5.915				
	25	5.915	8069	−28.1	−302.5	−65.5
	30	5.921				
	35	5.938				
75	15	6.398				
	20	6.392				
	25	6.396	8725	−31.5	−663.5	−86.3
	30	6.408				
	35	6.425				
90	15	7.225				
	20	7.225				
	25	7.238	9867	−36.8	−1115.3	−127.0
	30	7.252				
	35	7.279				

[a] Ref. 25, [b] Ref. 28.

The pK_a values of acetic acid at all the five temperatures increase as the proportion of the organic component in the medium increases, similar to the observations reported by us and also others for the variation of pK_a of acids of the type HA ($HA \rightarrow H^+ + A^-$) with change in the dielectric constant of the aquo-organic media[26]. For any composition of the medium, the pK_a values over the temperature range pass through a minimum[24]. For 90% methanol medium, the minimum is possibly at temperature lower than 15°. Ionisation of natural molecules into charged species according to Frank and Evans[27] accompany a decrease in entropy due

to the immobilization of a large number of solvent molecules around the charged species. In the present case, as expected, we find a decrease in entropy all through for the process. The entropy change is practically constant upto 30%. The small change around 45-50% methanol may be the result of the difference in electrostatic effects on the process[28]. This possibly indicates that upto 30% methanol, the solvation of ions is by water molecules and beyond 30% (may be 50%[28]) methanol, methanol molecules start competing with water molecules in the primary solvation sphere. The enthalpy-change for the dissociation process also passes through a maximum around 30% methanol, substantiating our assumption. ΔC_p° for the dissociation process decreases with increase in the percentage of the organic component. Similar decrease has been observed in case of dissociation of formic, acetic and propionic acids in dioxane-water media[25].

References

1. A. K. Basu and S. Aditya, *J. Indian Chem. Soc.*, 1971, **48**, 155.
2. A. K. Basu and S. Aditya, *Electrochim. Acta*, 1978, **23**, 1341.
3. A. K. Basu and S. Aditya, *Electrochim. Acta*, 1979, **24**, 275.
4. H. S. Harned and G. L. Kazanjian, *J. Am. Chem. Soc.*, 1936, **58**, 1912.
5. H. S. Harned and L. D. Fallon, *J. Am. Chem. Soc.*, 1939, **61**, 2377.
6. H. S. Harned, *J. Phys. Chem.*, 1938, 43, 275.
7. H. S. Harned and B. W. Ehlers, *J. Am. Chem. Soc.*, 1933, **55**, 2379.
8. H. S. Harned and T. R. Dedell, *J. Am. Chem. Soc.*, 1941, **63**, 3308.
9. H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, 1935, **57**, 1669.
10. A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, 1955, **20**, 747.
11. T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, 1956, **60**, 151.
12. M. Paabo, R. A. Robinson and R. G. Bates, *J. Chem. Eng. Data*, 1964, **9**, 374.
13. R. G. Bates, "Electrometric pH Determination : Theory and Practice", Willey, New York, 1954 p. 204.
14. R. G. Bates, "Electrometric pH Determination : Theory and Practice", Willey, New York, 1954, p. 112.
15. H. S. Harned and B. W. Ehlers, *J. Am. Chem. Soc.*, 1932, **54**, 1350.
16. W. J. Hamer, *J. Am. Chem. Soc.*, 1934, **56**, 860.
17. C. W. Davies, H. W. Jones and C. B. Monk, *Trans. Faraday Soc.*, 1952, **48**, 921.
18. V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 1958, 4144.
19. S. Chakraborty and S. Aditya, *J. Indian Chem. Soc.*, 1971, **48**, 493.
20. H. S. Harned and H. C. Thomas, *J. Am. Chem. Soc.*, 1935, **57**, 1666.
21. S. L. Melton and E. S. Amis, *J. Chem. Eng. Data*, 1968, **13**, 429.
22. R. A. Robinson and R. H. Stokes, "Electrolytic Solutions", 2nd. ed., Butterworths, London, 1959, p. 470, 475.
23. F. A. Long and W. F. McDevit, *Chem. Rev.*, 1952, **51**, 119.
24. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed., Reinhold, New York, p. 512.
25. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed., Reinhold, New York, p. 514.
26. S. K. Pal, U. C. Bhattacharyya, S. C. Lahiri and S. Aditya, *J. Indian Chem. Soc.*, 1969, 46, 497 ; S. C. Lahiri and S. Aditya, *Z. Physik. Chem.*, 1970, **244**, 351.
27. H. S. Frank and M. Evans, *J. Chem. Phys.*, 1945, **13**, 507.
28. M. Paabo, R. A. Robinson and R. G. Bates, *J. Am. Chem. Soc.*, 1965, **87**, 415.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 960-963

Thermodynamics of Acid Dissociation Equilibria of Some *N*-Substituted Anilinium Ions in Formamide

K. ACHARYA and B. NAYAK*

Department of Chemistry, Indian Institute of Technology Kharagpur-721 302

The acid dissociation constants of *N*-substituted anilinium ions have been determined accurately in formamide over the temperature range 10-50° (283.15-323.15 K) from the measurement of the e.m.f. of the cells,

Pt, H_2/B(m_1), BHCl(m_2)/AgCl-Ag.

The dissociation constants at 25° (298.15 K) have been checked by determining the same with the help of the cells,

Pt, Q-QH_2/B(m_1), BHCl(m_2)/AgCl-Ag.

Thermodynamical changes, $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the dissociation processes have been evaluated. The results show that the dissociation constants of these conjugate acids are in general lower (pK_a's higher) in formamide than their corresponding values in water.

IN our recent communications[1,2], we reported the acid dissociation constants of anilinium, nitroanilinium and bromoanilinium ions in formamide, a solvent of high dielectric constant (109.5) over the temperature range 10-50° (283.15-323.15 K) and related thermodynamical quantities as determined from e.m.f. measurements using cells of the type (A).

Pt, H_2/B(m_1), BHCl(m_2)/AgCl-Ag (A)

where B represents the base. It was also reported that the values of dissociation constants at 25° (298.15 K) as determined from the cells of the type (A) agree well with those obtained from e.m.f. measurements of cells of the type (B).

Pt, Q-QH_2 | B(m_1), BHCl(m_2) | AgCl-Ag (B)

The acid dissociation constants of *N*-methyl, *N*-ethyl, and *N*,*N*-dimethylanilinium ions in formamide, at several temperatures following the same procedure and using cells of the same types, are reported in this paper. This forms a part of the general programme in this laboratory to study different types of ionic equilibria in formamide, a solvent having a dielectric constant higher than that of water and a much wider liquid range.

Experimental

The aniline bases studied were all good quality products and were purified further by vacuum distillation. The hydrochlorides of the bases were prepared and purified by the standard procedures. The purity of the bases was checked by boiling point measurements and that of the hydrochlorides by titration. All the chemicals were stored in desiccators over Drierite until required. The bases and their hydrochlorides were handled in dry nitrogen atmosphere using a dry-box, the weighing of the compounds was performed using a closed weighing bottle which had been loaded in the dry-box. Formamide (L.R., S.D.'s) was purified as described[3] earlier.

The preparation of the solutions for e.m.f. measurements, filling and setting up of cells (A) and (B), thermostatting of the solutions and measurements of e.m.f. were all similar to those described earlier[1,4].

All measurements were reduced to 760 mm pressure. The vapour pressure of formamide was estimated to be less than 10 mm at temperatures below 60° (333.15 K) from data available in the literature. In most cases the correction for barometric pressure was found to be negligible.

Results and Discussion

As described in the earlier communication[1], the acid dissociation constant, K_a, of the conjugate acid is related to the e.m.f., E, of cells (A) and (B) through equation (1).

$$\frac{F(E-E°)}{2.303\,RT} + \log\frac{m(BH^+)m(Cl^-)}{m(B)} = -\log K_a - \log\frac{\gamma(BH^+)\,\gamma(Cl^-)}{\gamma(B)} \quad (1)$$

where E° is the standard e.m.f. of the cell, m and γ are, respectively, molalities and activity coefficients of the species shown in parentheses. Since $m(Cl^-) = m_2$, $m(BH^+) = m_2 - m(H^+)$, and $m(B) = m_1 + m(H^+)$, the second term of the left hand side of equation (1) was calculated from the experimental data when $m(H^+)$ was negligible compared to m_1 and m_2 as this becomes equal to $\log m_2^2/m_1$. The left hand side of equation (1), which may be represented by $-\log K'_a$, will vary with the ionic strength of the medium and will yield $-\log K_a$ when

TABLE 1—DETERMINATION OF $-\log K_a$ OF N-METHYLANILINIUM ION ($N\text{-MeAnH}^+$) IN FORMAMIDE AT 25° (298.15 K)

$10^3 m_1$ mol kg^{-1}	$10^3 m_2 = 10^3 \mu$ mol kg^{-1}	$\frac{E}{V}$	$\frac{F(E-E^0)}{2.303\,RT}$	$-\log \frac{m_2^2}{m_1}$	$-\log K_a'$	$-\log K_a$
From study of cell (A)						
0.665	0.412	0.6585	7.7777	2.5930	5.1847	
0.982	0.680	0.6445	7.5410	2.3044	5.2366	
1.228	0.764	0.6415	7.4908	2.3280	5.1673	5.26
1.043	0.918	0.6228	7.1742	2.0926	5.0816	±0.04
1.296	1.052	0.6244	7.2013	2.0686	5.1327	
1.418	1.262	0.6162	7.0627	1.9496	5.1131	
From study of cell (B)						
0.925	0.616	−0.0515	7.6732	2.3870	5.2862	
0.898	0.702	−0.0700	7.5295	2.2606	5.2689	
1.236	0.852	−0.0788	7.4653	2.2811	5.2342	5.33
1.076	1.005	−0.0935	7.1328	2.0275	5.1048	±0.06
1.480	1.226	−0.0878	7.2287	1.9933	5.2354	
1.596	1.318	−0.0915	7.1661	1.9632	5.2029	

TABLE 2—DETERMINATION OF $-\log K_a$ OF N-ETHYLANILINIUM ION ($N\text{-EtAnH}^+$) IN FORMAMIDE AT 25° (298.15 K)

$10^3 m_1$ mol kg^{-1}	$10^3 m_2 = 10^3 \mu$ mol kg^{-1}	$\frac{E}{V}$	$\frac{F(E-E^0)}{2.303\,RT}$	$-\log \frac{m_2^2}{m_1}$	$-\log K_a'$	$-\log K_a$
From study of cell (A)						
0.708	0.328	0.6815	8.1665	2.8183	5.3482	
0.926	0.437	0.6771	8.0921	2.6856	5.4065	
1.088	0.516	0.6694	7.9620	2.6113	5.3507	5.47
1.385	0.743	0.6536	7.6949	2.3995	5.2954	±0.03
1.640	0.908	0.6410	7.4819	2.2987	5.1832	
1.882	1.075	0.6376	7.4244	2.2001	5.2243	
From study of cell (B)						
0.813	0.406	−0.0348	8.1246	2.6930	5.4316	
1.165	0.613	−0.0506	7.8575	2.4914	5.3661	
1.408	0.732	−0.0575	7 7408	2.4196	5.3212	5.57
1.551	0.844	−0.0683	7.5583	2.3379	5.2204	±0.03
1.793	0.917	−0.0670	7.5803	2.3288	5.2515	
2.066	1.139	−0.0779	7.8960	2.2021	5.1939	

TABLE 3—DETERMINATION OF $-\log K_a$ OF N,N-DIMETHYLANILINIUM ION ($N,N\text{-Me}_2\text{AnH}^+$) IN FORMAMIDE AT 25° (298.15 K)

$10^3 m_1$ mol kg^{-1}	$10^3 m_2 = 10^3 \mu$ mol kg^{-1}	$\frac{E}{V}$	$\frac{F(E-E^0)}{2.303\,RT}$	$-\log \frac{m_2^2}{m_1}$	$-\log K_a'$	$-\log K_a$
From study of cell (A)						
0.790	0.234	0.6985	8.4539	3.1592	5.2947	
1.136	0.408	0.6704	7.9789	2.8341	5.1448	
1.084	0.562	0.6556	7.7287	2.5356	5.1931	5.40
1.448	0.705	0.6425	7.5072	2.4644	5.0428	±0.04
1.780	0.768	0.6402	7.4684	2.4797	4.9887	
1.915	0.835	0.6388	7.4447	2.4388	5.0059	
From study of cell (B)						
0.986	0.325	−0.0226	8.3308	2.9701	5.3607	
0.872	0.416	−0.0424	7.9961	2.7023	5.2938	
1.558	0.604	−0.0535	7.8085	2.6305	5.1780	5.53
1.392	0.685	−0.0705	7.5211	2.4723	5.0488	±0.04
1.608	0.772	−0.0718	7.4991	2.4311	5.0680	
1.990	0.926	−0.0776	7.4011	2.3657	5.0354	

trapolated to zero ionic strength, the ionic ·ength of the solution, μ, being given by m_2.

The pK_a values obtained by this procedure over e temperature range 10-50° (283.15-323.15 K) are shown in Table 4 alongwith the standard deviations calculated by the method of least squares. Typical e.m.f. readings of cells (A) and (B) and other data needed for the computation of $-\log K_a$ at 25° (298.15 K) are shown in Tables 1-3.

TABLE 4—EFFECT OF TEMPERATURE ON $-\log K_a$ FROM STUDY OF CELL (A) IN FORMAMIDE

Temp. °C	$-\log K_a$		
	N-MeAnH$^+$	N-EtAnH$^+$	N,N-Me$_2$AnH$^+$
10	5.38 ± 0.06	5.61 ± 0.02	5.65 ± 0.06
15	5.28 ± 0.04	5.68 ± 0.03	5.48 ± 0.05
20	5.26 ± 0.05	5.55 ± 0.02	5.50 ± 0.05
25	5.26 ± 0.04	5.47 ± 0.03	5.40 ± 0.04
	(5.33 ± 0.06)*	(5.57 ± 0.08)*	(5.58 ± 0.04)*
30	5.14 ± 0.03	5.38 ± 0.01	5.28 ± 0.05
35	4.94 ± 0.05	5.26 ± 0.03	5.20 ± 0.07
40	5.05 ± 0.03	5.27 ± 0.02	5.19 ± 0.09
45	4.96 ± 0.03	5.18 ± 0.02	5.00 ± 0.05
50	4.88 ± 0.05	5.15 ± 0.03	5.09 ± 0.04

* Values in parentheses from study of cell (B).

A comparison of the present pK_a data with the corresponding values in water is not possible because of the lack of relavant data in water at all temperatures. However, available data at 25° (298.15 K) (Table 5) show that pK_a values are higher in formamide than in water which is in complete agreement with our previous observations[1,2] and with the general behaviour of the conjugate acids of bases and of weak acids in solvents of this class[4-8]. The pK_a values obtained for these conjugate acids at 25° (298.15 K) with cell (B) are slightly higher than those obtained with cell (A) (Table 4). Taking the limitations of the quinhydrone electrode in media containing amines into consideration, this agreement is quite satisfactory and confirms our earlier suggestion[1,2] that quinhydrone electrode behaves more satisfactorily in formamide than in water, even in the presence of amines.

A comparison of the pK_a values of these conjugate acids at 25° (298.15 K) in different solvents (Table 5) shows that in general, the pK_a values are not linearly related to 1/D (where D is the dielectric constant of the medium) as suggested by Born equation, although they seem to depend, to a large extent, on the dielectric constant of the medium. The fact that the pK_a values of these conjugate acids are higher in formamide than in water even though the latter has a lower dielectric constant, may be due to the lower basicity of formamide compared to that of water as already suggested[9].

TABLE 5—pK_a VALUES OF ANILINIUM IONS IN DIFFERENT SOLVENTS AT 25° (298.15 K)

Ion	Water[b] D=78.54	Formamide[a] D=109.5	Nitromethane[c] D=35.9	Acetic acid[d] D=6.2
N-MeAnH$^+$	4.85	5.26	—	2.67
N-EtAnH$^+$	5.11	5.47	—	2.83
N,N-Me$_2$AnH$^+$	5.06	5.40	11.04	2.86
AnH$^+$	4.58	5.10[e]	9.07	—

[a] Present work, [b] Ref. 10, [c] Ref. 11, [d] Ref. 12, [e] Ref. 1.

As expected, the increase of temperature has a general effect of lowering the pK_a values of these conjugate acids (Table 4). However, in agreement with the earlier studies, irregularities are noticed for which there is no ready explanation. As has been suggested earlier[1,2], these might be due to minute structural changes occurring in the hydrogen bonded solvent with the change of temperature.

The thermodynamic properties, ΔG°, ΔH° and ΔS° have been evaluated as described earlier[1] on the assumption that ΔH° does not change appreciably over the temperature range used. The plots of $\log K_a$ *vs* 1/T are linear in all the cases, thereby implying that the assumption is reasonable. The results are shown in Table 6 alongwith those for anilinium ion, but a comparison with the results in aqueous medium is not possible due to the lack of relevant data in the literature.

TABLE 6—STANDARD THERMODYNAMIC VALUES FOR DISSOCIATION PROCESS $BH^+ \rightleftharpoons B + H^+$ IN FORMAMIDE AT 25° (298.15 K)

Base (B)	ΔG° kJ mole^{-1}	ΔH° kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}
N-Methylaniline	30.03	21.41	−28.91
N-Ethylaniline	31.23	23.88	−24.65
N,N-Dimethylaniline	30.83	26.18	−15.60
Aniline	29.11*	27.28*	−6.14*

* Ref. 1.

These results show that ΔG° values of the dissociation processes for anilinium and N-substituted anilinium ions in formamide appear in the order,

$$AnH^+ < N\text{-}MeAnH^+ < N,N\text{-}Me_2AnH^+ < N\text{-}EtAnH^+,$$

which is similar to that found in aqueous medium on the basis of pK_a data shown in column 1 of Table 5. It is further found that in formamide medium ΔH° values appear in the order,

$$N\text{-}MeAnH^+ < N\text{-}EtAnH^+ < N,N\text{-}Me_2AnH^+ < AnH^+.$$

The relative orders of ΔH° between N-MeAnH$^+$ and N-EtAnH$^+$ and between N-MeAnH$^+$ and N,N-Me$_2$AnH$^+$ are quite expected from the standpoint of the inductive effects of the groups attached to the nitrogen atom. As is well known, the ethyl group will exert a larger inductive effect than the methyl group and the combined inductive effect of two methyl groups will be obviously greater than that of a single methyl group. However, when these ΔH° values for N-substituted anilinium ions are compared with that for the anilinium ion, the foregoing rule seems to breakdown completely. The relative acidity of these anilinium ions, therefore, can not be explained on the basis of the inductive effects of the groups attached to the nitrogen atom as is commonly done. The reason for their apparent order lies elsewhere as can be seen from the ΔS° values for the dissociation processes. These values appear in the order,

$$N\text{-}MeAnH^+ < N\text{-}EtAnH^+ < N,N\text{-}Me_2AnH^+ < AnH^+,$$

which is the same as that for the ΔH° values also. But when these two sets of values are combined through the relation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, the ΔG° values appear in a different order as discussed above.

Thus, in reality, ΔG^o values of these anilinium ions are much more complicated functions of substrate and solvent properties as reflected through their corresponding ΔH^o and ΔS^o values and any effort to correlate these with either substrate or solvent properties alone would be generally futile.

References

1. K. ACHARYA and B. NAYAK, *Electrochim. Acta*, 1983, **28**, 1041.
2. K. ACHARYA and B. NAYAK, *Thermochim. Acta*, 1983, **66**, 377.
3. U. N. DASH and B. NAYAK, *Indian J. Chem.*, 1970, **8**, 659.
4. S. MUKHOPADHYAY and B. NAYAK, *Electrochim. Acta*, 1980, **25**, 807.
5. S. MUKHOPADHYAY and B. NAYAK, *Thermochim. Acta*, 1980, **40**, 433.
6. U. N. DASH and B. NAYAK, *Aust. J. Chem.* 1975, **28**, 793.
7. U. N. DASH and B. NAYAK, *Aust. J. Chem.*, 1972, **25**, 941.
8. U. N. DASH and B. NAYAK, *Aust. J. Chem.*, 1973, **26**, 111.
9. U. N. DASH and B. NAYAK, *Aust. J. Chem.*, 1975, **28**, 1377.
10. A. ALBERT and E. P. SERJEANT, "Ionization Constants of Acids and Bases", Methuen, London, 1962, p. 144.
11. B. A. KOROLEV and B. I. STEPANOV, *Izv. Vys. Ucheb Zaved. Khim. Khim. Tekhnol.*, 1968, **11**, 1193.
12. N. F. HALL, *J. Am. Chem. Soc.*, 1930, **52**, 5115.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 964-966

Effect of Sugars on CMC of Aqueous Solution of Cetyltrimethylammonium Bromide

S. K. KANUNGO and B. K. SINHA*

P. G. Department of Chemistry, Sambalpur University, Jyoti Vihar-768 019

The effect of glucose, fructose and sucrose on the critical micelle concentration (CMC) of a cationic surfactant, *i.e.* cetyltrimethylammonium bromide (CTAB) has been studied conductometrically at 35°. It has been observed that on addition of varying concentration of D-glucose and sucrose (0.05-0.3 *M*) the CMC of CTAB increases. The first CMC of CTAB in pure water is found to be 9.0×10^{-4} *M* at 35° by this method. However, in presence of varying concentration of D-fructose the CMC decreases initially and then increases.

A close review of literature indicates that the effect of additives has been studied on the CMC of surfactants by many workers[1-10]. Effect of co-solvents on thermodynamics of aggregation of surfactants in aqueous solutions has also been examined[11,12]. Blandamer *et al.*[13] have found that by addition of glucose, fructose and arabinose to the micellar catalysed reaction of 2,4-dinitrochlorobenzene with hydroxide ions, the first order rate constant increases, indicating an enhancement of the catalytic action of CTAB. But they have mentioned that attempts to measure the effect of sugar on the CMC of CTAB proved unsuccessful. In fact there is hardly any study on the effect of sugar on the CMC of surfactants and this enthuse us to take up this problem. Recently we have communicated[14] our findings on the change of CMC of an anionic surfactant, sodium dodecyl sulphate (NaLS) by addition of sugars.

Experimental

Cetyltrimethylammonium bromide (B.D.H., England) was purified by the method of Duynstee and Grunwald[15]. D-glucose, D-fructose and sucrose were of E.M. reagent grade and used without further purification. All the solutions were prepared in triple-distilled water.

In order to prepare good number of solutions of varying concentration of CTAB (of the order of 10^{-4}*M*) maintaining a fixed concentration of sugar in it, different volumes of CTAB and sugar solutions of appropriate concentrations were mixed and diluted with triple-distilled water. The specific conductance of these solutions were measured at 35° putting the conductivity cell in a thermostat using Systronics 304 digital direct reading conductivity meter. Then graphs were plotted with [CTAB] *vs* specific conductance. The CMC value was found out from the break point on the graph. CMC of CTAB in the absence and presence of a series of sugar concentrations were determined similarly and different sugars tried.

Results and Discussion

The first CMC of CTAB in pure water at 35° was found to be 9.0×10^{-4}*M* and increased gradually by the addition of different quantities of glucose and sucrose, but when fructose was added the CMC decreased and then increased slowly (Table 1). The concentration of sugars have been varied from 0.05 to 0.3 *M* and the experimental CMC values are given

TABLE 1—VARIATION OF CMC OF CTAB IN AQUEOUS SUGAR SOLUTIONS OF VARYING CONCENTRATION AT 35°

Additive *M*	CMC $\times 10^4$ *M*	ΔG°_{m} kcal mol^{-1}
Nil	9.0	7.37
D-Glucose		
0.10	9.2	7.36
0.15	9.4	7.345
0.20	9.6	7.33
0.25	10.0	7.30
0.30	12.0	7.19
D-Fructose		
0.05	6.5	7.56
0.10	7.0	7.52
0.20	8.0	7.44
0.25	8.4	7.41
0.30	8.6	7.40
Sucrose		
0.05	10.4	7.28
0.10	12.0	7.19
0.15	12.8	7.15
0.20	13.8	7.09
0.30	15.6	7.04

in Fig. 1, which shows the molar CMC of CTAB at 35° as a function of molarity of the organic additive, the sugars. In case of NaLS, addition of all these sugars have shown rise in the CMC values and it is in the order, D-fructose > sucrose > D-glucose[14]. But in case of CTAB, some differences were noted. By addition of D-fructose, instead of

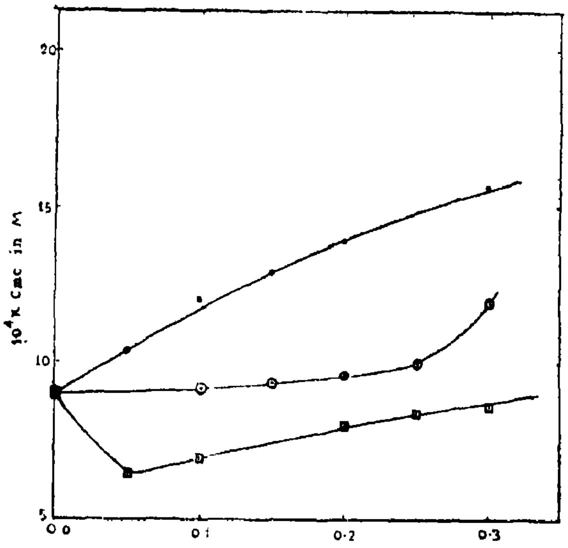


Fig. 1. CMC's for CTAB in aqueous sugar solutions at 35°: ●, sucrose ; ⊙, glucose ; ⊡, fructose.

increase of CMC of CTAB it decreased, whereas sucrose and D-glucose have maintained the same trend as in case of NaLS. The latter sugars at 0.3 *M* concentration have raised the CMC of NaLS about 3 and 5 times whereas the corresponding values with CTAB are about 1.33 and 1.50 times, respectively.

The effects of various sugars on the CMC are displayed in a somewhat different manner in Fig. 2, *i.e.* as $-RT\ln X_0$ *vs* mole-fraction of sugars, where X_0 represents the CMC in mole-fraction units. For calculating the mole-fractions the volume of solutes have not been taken into consideration. Blandamer *et al.*[18] have observed a dramatic rate enhancement by the effect of added fructose in the reaction

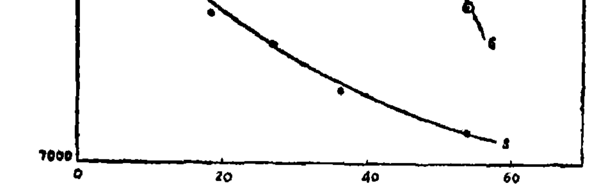


Fig. 2. Stability of CTAB micelles in aqueous sugar solutions at 35°: ⊡, fructose ; ⊙, glucose ; ●, sucrose.

mentioned earlier. But by addition of fructose the CMC decreases in our case. However, they have carried on their kinetic studies in more diluted solution of sugars (*ca.* 10 times) and concentrated solution of CTAB (*ca.* 10 times) in comparision to our work.

Emerson *et al.*[1] have observed that addition of sucrose to aqueous solution of a cationic surfactant increases the CMC but they have not focussed their attention in particular on sucrose so far their discussion is concerned. In general, they have suggested the increase of CMC is due to the breaking of micelles and penetration of additives. They have also explained it taking thermodynamic parameters into account. There are also additives which are non-penetrating in nature but still influence the aggregation of surfactants.

The values of ΔG°_m have been computed from $-RT\ln X_0$ and have been given in Table 1. It is the standard free energy of transfer of a monomer from aqueous phase to an aggregate which already contains the number of monomers at the CMC, *i.e.* to a micelle of average size $\bar{m}$. In case of D-fructose at 35°, $\Delta G^\circ_{\bar{m}}$ values are more negative and, hence, more stable is the micelle, under the experimental condition in comparison to D-glucose and fructose.

The effect of additives on CMC can be discussed in term of the change in water structure. The formation of the so-called iceberg structure around the hydrocarbon chains of surfactant molecules bring about a loss of entropy at their dissolution. For charged micelles thermodynamic parameters are complex, since they represent a composite of hydrophobic and electrostatic interactions. Sugars are water-structure makers and due to the presence of more number of hydroxy groups sucrose is a better structure-maker than glucose and fructose. In case of CTAB micelle the head groups will be strongly hydrated in the presence of sugars. Sugars being dipolar in character, it may so happen, that some of the water molecules around the positive head group may be replaced by sugar molecules as a result of which the electrostatic interaction between the head group and counter-ion decreases. Under such situation, the CMC of CTAB increases when sugar concentration is increased. An increase in the CMC may be partly due to the increase in the number of free counter-ions for adsorption of sugar molecules in the Stern layer of the surfactant micelle.

Gratzer and Beaven[4] have marked the CMC decrease to small extent by addition of sucrose in case of a nonionic surfactant where it can be explained only on the basis of hydrophobic interactions since electrostatic interactions are not involved. In the present study, CMC of CTAB decreases by the addition of fructose only. It seems, all the factors controlling the CMC including concentration of CTAB and its cationic nature and the concentration of fructose and its structure making character are

ideal for which the CMC decreases where the structure making character has predominated.

The CMC increase observed in case of sucrose is more than that of glucose as sucrose is a better structure-maker than glucose for having more number of hydroxy groups and its bulky structure. The system of CTAB, sugar and water is extremely complex. Hence, to offer explanation for the interactions of these hydrophilic sugars becomes difficult and further study in this line is in progress.

Acknowledgement

Our sincere thanks are due to Prof. G. B. Behera, Sambalpur University for his valuable suggestions and keen interest in ihe progress of the work.

References

1. M. F. EMERSON and A. HOLTZER *J. Phys. Chem.*, 1967, **71**, 3320.
2. M. MIURA and M. KODAMA, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 428.
3. M. KODAMA, R. BOKU, T. ISHIDA and M. MIURA, *Bull. Chem. Soc. Jpn.*, 1977 **50**, 751.
4. W. B GRATZER and G. H. BEAVEN, *J. Phys. Chem.*, 1969, **73**, 2270.
5. L. MAGID in "Solution Chemistry of Surfactants", ed. K. MITTAL, Plenum Press, New York, Vol. 1, 1979.
6. H. N. SINGH and S. SWARUP, *Bull. Chem Soc. Jpn.*, 1978, **51**, 1534.
7. K. HAYASE and S. HAYANO, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 933.
8. M. MANABE and K. MASAHARU, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1599.
9. L. G. IONESCU, T. TOKUHIRO and B. J. CZERNIAWSKI, *Bull. Chem. Soc. Jpn.*, 1979 **52**, 922.
10. H. N. SINGH, S. SWARUP, R. P. SINGH and S. M. SALEEM, *Indian J. Chem., Sect. A*, 1981, **20**, 292.
11. J. E. ADDERSON and C. G. BUTLER, *J. Pharm. Pharmacol.*, 1972, **24**, 130.
12. G. C. KRESHECK and W. A. HARGHAVES, *J. Colloid Interface Sci.*, 1974, **48**, 481.
13. M. J. BLANDAMER, G. H. BEATHAM, C. H. BRANCH and D. J. REID, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 2139.
14. G. DEO, L. N. PANDA and B. K. SINHA, *Acta Ciencia Indica*, communicated.
15. E. F. DUYNSTEE and E. GRUNWALD, *J. Am. Chem. Soc.*, 1959, **81**, 4540, 4542.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 967-968

Role of Defects in Recovery of Radiolytic Damage in Irradiated Potassium Nitrate

B. M. MOHAPATRA and D. BHATTA*

Department of Chemistry, Utkal University, Bhubaneswar-751 004

The role of lattice defects introduced by doping and crushing in the thermal annealing of γ-irradiated potassium nitrate as well as the effect of crushing in the recovery process of doped (Ba^{2+}) crystals has been studied. It is seen that the doped crystals are more susceptible to recovery than the pure substance above the temperature of 400 K crystal transition (rhombic $\rightleftharpoons$ trigonal). The data show that in both the substances crushing prior to irradiation enhances the rate of recovery, whereas subsequent to irradiation lowers the rate.

A crystalline substance ordinarily contains a fair concentration of defects such as interstitials and vacancies. Further defects are introduced by crushing, compression, doping, fast neutron bombardment[1-7], *etc.* The influence of defects on the initial damage and in the subsequent recovery of damage species has been studied by many workers[8-10]. It is interesting to have a comparative study of annealing in pure and doped (Ba^{2+}) potassium nitrate, also the effect of crushing prior and subsequent to irradiation on the recovery process of those crystals.

Experimental

Doped crystals (1.0 mol %) of potassium and barium nitrate (A.R., B.D.H.) were prepared following the standard procedure[11]. The mixed crystals were cooled in a desiccator, crushed in an agate mortar and dried at 383 K for 10 h. Irradiation was carried out in glass ampoules at room temperature with cobalt-60 γ-rays to a dose of 6.0×10^{-1} MGY at the dose rate of 0.102×10^{-2} MGY h^{-1}. A portion of the pure as well as doped crystals was crushed into fine powder prior and subsequent to irradiation. The damage nitrite wrs estimated spectrophotometrically by diazocolour reaction[12,13]. Isothermal recovery studies in pure and doped crystals were carried out between 403 to 433 K and in crushed substances at 423 K by following the procedure described elsewhere[10].

Results and Discussion

The colours of the crystals were not much affected by irradiation and the damage induced in pure and doped (Ba^{2+}) potassium nitrate by cobalt-60 gamma-rays are respectively 66.49 and 63.27 μ mol NO^-_2 g^{-1}. The lower initial damage in the doped crystals than in the pure salt may be ascribed[14] to competition between dopant (Ba^{2+}) and the radiolytic damage fragments for the electrons involved in the radiation chemical processes. The data show (Fig. 1) that both the crystals undergo an abrupt recovery above the temperature of 400K crystal transition (rhombic $\rightleftharpoons$ trigonal). The susceptibility of doped crystals to thermal recovery than the pure salt is due to the generation of cationic vacancies[15,16] in the crystal lattice of potassium nitrate by the divalent Ba^{2+} which increases the free space and consequently accelerates the migration of the mobile fragments. Direct recovery induced in the pure crystals by crushing is negligible, whereas very low value ($\varphi=0.022$) is obtained in doped crystals.

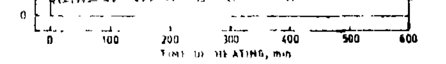


Fig. 1. Annealing of nitrite in gamma-irradiated pure and doped (Ba^{2+}) potassium nitrate.

TABLE 1—EFFECT OF CRUSHING IN THE THERMAL ANNEALING OF PURE AND DOPED (Ba^{2+}) POTASSIUM NITRATE

Substance	Untreated	Crushed prior to irradiation	Crushed subsequent to irradiation
	Fraction annealed, φ		
KNO_3	0.092	0.159	0.048
$KNO_3(Ba^{2+})$	0.791	0.822	0.651

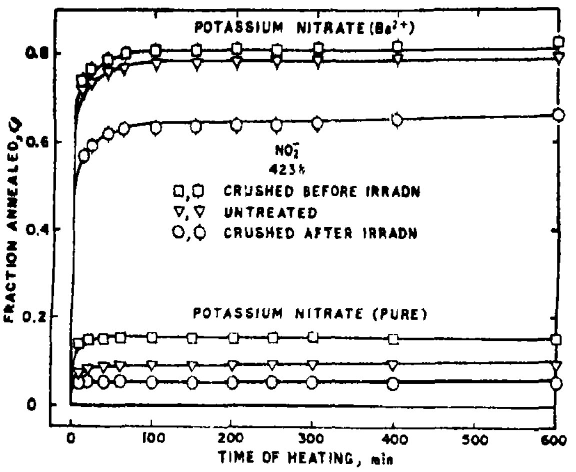


Fig. 2. Influence of crushing on isothermal annealing in gamma-irradiated pure and doped (Ba^{2+}) potassium nitrate.

It is seen that in both pure as well as doped crystals, crushing prior to irradiation enhances the rate of recovery, whereas subsequent to irradiation retards the process. During crushing an activated creep or plastic flow process[6,17-19] occurs in the crystal lattice generating vacancies and interstitials, which causes local strain[20] in the lattice resulting decrease in the activation energy for the migration of the mobile fragments (NO_2^- or O_2/O) towards the other stationary species (O_2/O or NO_2^-). The consequent increase in the jump-frequency results in direct recovery and in the higher rate of thermal annealing is observed. The local strain produced also lowers the potential[5,8] barrier for the release of the trapped fragments more possibly O_2, thereby contributing to the direct recovery. The obove phenomenon occurs in the crystals subjected to crushing prior to irradiation. The rate and magnitude of annealing in both the crystals is lower than the untreated salts when crushing is carried out after irradiation. During crushing the trapped oxygen (O_2) is released and escape out of the crystal lattice causing low recovery.

References

1. S. R. MOHANTY and S. R. UPADHYAY, *Nature (London)*, 1963, **199**, 169; 1964, **201**, 921.
2. T. ANDERSEN, *Nature (London)*, 1963, **200**, 1094.
3. M. KHARE and S. R. MOHANTY, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1527.
4. M. KHARE and S. R. MOHANTY, *Radiochim. Acta*, 1967, **8**, 68.
5. S. R. MOHANTY and S. M. K. NAIR, *Radiochim. Acta*, 1970, **13**, 87.
6. T. ANDERSEN and A. G. MADDOCK, *Trans. Faraday Soc.*, 1963, **59**, 2362.
7. T. ANDERSEN, *Trans. Faraday Soc.*, 1963, **59**, 2625.
8. S. R. MOHANTY and V. M. PANDEY, *J. Sci. Ind. Res.*, 1975, **34**, 196.
9. D. BHATTA, S. R. MOHANTY and K. C. SAMANTRAY, *Radiochim. Acta*, 1981, **28**, 13.
10. B. M. MAHAPATRA and D. BHATTA, *Indian J. Chem., Sect. A*, 1984, **23**, 512.
11. V. V. BOLDYREV, V. M. LYKHIN, A. N. OBLIVANTSEV and K. M. SALIKHOV, *Kinet. Catal.*, 1966, **7**, 383.
12. M. B. SHINN, *Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 33.
13. N. F. KERSHAW and N. S. CHAMBERLIN, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 312.
14. V. V. GROMOV, *Russ. Chem. Rev. (Engl. Transl.)*, 1974, **43**, 201.
15. J. CUNNIGHAM in "Radical Ions", eds. K. T. KAISER and L. KEVAN, Interscience, New York, 1968, p. 475.
16. YU. A. ZAKHAROV and E. P. ABAKUMOV, *ISZ. Tomsk. Politekh. Inst.*, 1970, **176**, 10.
17. F. SEITZ, *Phys. Rev.*, 1950, **80**, 239.
18. F. C. FRANK and W. T. READ, *Phys. Rev.*, 1950, **79**, 722.
19. F. SEITZ, *Adv. Phys.*, 1952, **1**, 43.
20. A. W. OVERHAUSER, *Phys. Rev.*, 1953, **90**, 393.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 969-972

A Quantum Mechanical Approach to the Theory of Cancer from Polynuclear Molecules. Metabolic Activation and Carcinogenicity of Methylphenanthrenes

S. NOOR MOHAMMAD

Molecular Biology and Biophysics Programme, Department of Physics and Meteorology,

Indian Institute of Technology, Kharagpur-721 302

Metabolism and cancer-inducing ability of methylphenanthrenes are determined using quantum mechanical method in the MINDO/3 approximations of Bingham *et al.* Several reactivity and molecular parameters are used for the purpose. Results of the calculations indicate that none of the isomeric methylphenanthrenes are active as cancer initiator and that 1,2-diol-3,4-epoxide which is the ultimate metabolite for each of them is very weak. The predictions are in striking agreement with the experiment.

THE rapid increase in the number of known chemical carcinogens[1,2] from one (dibenz(a,h)anthracene) in 1929 to several hundreds at the present time has opened up unparallel scope of developments in the study of chemical carcinogens. Recently it has become apparent that many chemical carcinogens including PAHs require metabolic activation[3,4] in order to be able to react with cellular macromolecules and exert their biological effects. There are a number of techniques for the study of metabolic activations and various strains on which these methods can be applied. So far, works have been carried out in whole animals[5], in cells in culture[6,7], in tissues in short term organ cultures[8], and in tissue preparations derived from a variety of sources[9]. There are differences in the products obtained from various types of experiments. However, the overall pattern of metabolites in all the cases is the same. When a PAH is metabolized a number of isomeric dihydrodiols are theoretically formed on the peripheral double bonds throughout the molecule. These dihydrodiols are next metabolized to diol-epoxides either by metabolism at adjacent olefinic double bonds or at aromatic bonds in other rings of the molecule. In the case of methylated hydrocarbons, the hydroxylation of methyl group(s) may also occur, which increases the possible number of dihydrodiols/diol-epoxides.

The substitution of methyl group for hydrogen at various positions of the aromatic ring structures of PAHs changes their carcinogenic activities[5,10,12]. These changes seem to stem from steric interactions in which the methyl group alters the electronic distributions of the molecule. Methyl group is electron donor and is able to provide additional charge for the aromatic backbone of the methylated PAH. Incidentally, there is an alternative possibility in which no charge is migrated from the methyl group but an enhanced conjugation takes place. A situation can also arise in which one can think of superposition of both the possibilities. Whatever be the mechanism, the net effect is that the methylation modifies the metabolic processes, and yields either a highly reactive dihydrodiol (diol-epoxide), or deactivates the compound.

In recent years a number of workers have carried out investigations on the carcinogenic activities of methylated PAHs. The compounds include BP, BA, chrysene, phenanthrene and fluoranthrene[5,10-12]. Using a two stage procedure to initiate skin tumors in mice Iyer *et al.*[10] have found that 11-MBP is about three times as active as the parent compound. In the case of BA 7-MBA exhibits much higher carcinogenicity than the BA itself[5]. Chrysene is almost inactive, but 5-methylchrysene is highly carcinogenic[13]. Recent observations[14] indicate that this compound, when tested on animals, shows carcinogenicity equivalent to that of BP. Phenanthrene is perhaps the only compound in which methylation does not induce any change of carcinogenicity. LaVoie *et al.*[11,15] heve determined the mutagenicity, *in vitro* metabolism, and tumor initiating ability of MePs. Similar to the parent compound (Fig. 1) none of the methyl derivatives was found active on the mouse skin.

We are in the process of developing the theory of carcinogenicity of polycyclic hydrocarbons using

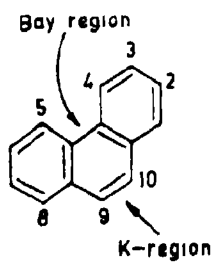


Fig. 1. Molecular structure of phenanthrene.

Abbreviations: PAH, polycyclic aromatic hydrocarbon; BP, benzo(a)pyrene; BA, benz(a)anthracene; MBA, methylbenz(a)anthracene; MBP, methylbenzo(a)pyrene; MeP, methylphenanthrenes.

self-consistent-field (SCF) molecular orbital (MO) method. The theory is applied to alternant hydrocarbons[15,16], non-alternant hydrocarbons (fluoranthrene)[17], MBAs[18], MBPs[19], and methylchrysenes[20] with striking success. The purpose of the present paper is to examine the applicability of the theory to MePs.

Outline of theoretical method :

There are diversity in the characteristics of PAHs. In view of this and that there are many factors involved in the modifications of biological activities, no single chemical or physical properties can be fully correlated with the carcinogenicity of the compounds. Our theory makes use of a number of molecular properties and reactivity indices in an effort to elucidate various aspects of carcinogenic characteristics of the compounds.

The theory is based on the all-valence electron-SCF-MO method with MINDO/3 approximations of Bingham *et al.*[21]. Due to molecular symmetry there are only five unique monomethyl derivatives of phenanthrene. The relatively narrow range of activity exhibited by these derivatives requires that these materials be tested under identical conditions in order to produce meaningful results for comparison. It is obviously very difficult to achieve the exact identical conditions. In order to keep scope for considerations in case any inconsistency results from the non-satisfaction of ideal conditions we carried out calculations for all the MePs. In the MO methods the results are highly sensitive to the choice of geometry of the test molecules. Using a stepwise optimization procedure we optimized the geometry of phenanthrene in an earlier paper[15] of the series. In the present investigation this geometry is adopted as the fixed skeleton backbone, except that the methyl groups substituted for the hydrogen atoms are individually optimized. Fletcher-Powell-Davidon minimization technique[22,23] is applied for optimization.

Results and Discussion

In earlier investigations[15-20] we considered $R_{AB}(\pi)$, $R_L(\pi)$, $R_t(\pi)$ and E_{AB} as possible indices for the metabolic activation of PAHs. $R_{AB}(\pi)$ and E_{AB}, among them, came out as the most effective indices. In the present investigation we confine ourselves only to these indices. The values V_{1k} of $R_{AB}(\pi)$ and V_{2k} of E_{AB} corresponding to various peripheral/terminal bonds k (k = 1, 2, 3, 4) of MePs are listed in Table 1. Results for the bridgehead unreactive carbon atoms and bonds are not however presented in the Table. The calculations have been carried out in the double precision to ensure that the presented data are accurate at least up to four decimal places. According to our earlier classifications MePs having bay-regions are group I molecules in which the ultimate metabolite should be a bay-region diol-epoxide. If we rearrange V_{jk} (j = 1, 2) in the decreasing order, *viz.* to V_{j1} (*e.g.* $V_{j1} > V_{j2} > V_{j3}$ ..) the bond X_{11} corresponding to V_{11} would represent the site of dihydrodiol ; that (*e.g.* X_{21}) corresponding to V_{21} to the site of epoxide. The bond

TABLE 1—CALCULATED BOND REACTIVITY INDICES[a] OF METHYLPHENANTHRENES

Location of methyl group	Bond (A – B) 1 – 2	3 – 4	5 – 6	7 – 8	9 – 10
1	0.1144 20.879	0.1144 20.867	0.1168 21.887	0.1160 21.869	0.1178 21.576
2	0.1145 20.852	0.1146 20.852	0.1170 21.876	0.1161 21.527	0.1182 21.579
3	0.1143 20.879	0.1143 20.867	0.1161 21.869	0.1167 21.922	0.1178 21.586
4	0.1140 20.875	0 1141 20.700	0.1159 21.018	0.1170 21.895	0.1174 21.590
5	0.1142 20.869	0.1142 20.863	0.1169 21.914	0.1169 21.940	0.1170 21.837

[a] Upper and lower results in each row correspond to $-R_{AB}(\pi)$ and $-E_{AB}$(eV), respectively.

X_{12} with energy V_{12} which belongs to bay-region would represent the site of epoxidation. In the case of E_{AB} the bond X_{22} belongs to region distal to the bay and represents the site of dihydrodiol. From Table 1 it is apparent that the values of $R_{AB}(\pi)$ for all of the MePs are extremely insensitive to the choice of bond. This implies that no effective metabolite results from the biological activation of the molecules, or conversely, the metabolites are formed, but are very weak, and are unable to initiate cancer. The implication is consistent with our observations in the earlier investigation[18] which is completely in agreement with the experiments. The distribution of predicted metabolites is summarized in Table 2. For all MePs the predicted ultimate metabolite is 1,2-diol-3,4-epoxide with epoxide formed in the bay-region and the diol in region distal to it. The 9,10-bonds of MePs correspond to the K-regions. The predicted metabolite of this bond, according to our postulates, is an oxide (or dihydrodiol). One fudamental hypothesis of the K-region theory of Pullman and Pullman[24] is that the interaction between the carcinogen and cellular receiver takes place through the K-region of the carcinogen. The interaction is of electrostatic nature and is effective when an oxide is formed in the K-region. Contrary to the assumptions of Pullman and Pullman, results in Table 2 indicate that the K-region oxides are the least reactive and can not be related to cancer.

As an attempt to explain the carcinogenic strengths various molecular properties of MePs are listed in Table 3. Almost identical results for 1- and 8-, 2- and 7-, 3- and 6-, and 4- and 5- MePs which are equivalent indicate that the geometry is constructed quite consistently. Table 3 includes energies of the highest occupied MO (HOMO)(say, the nth.MO), E_{Hl}, and of the lowest unoccupied MO (LUMO) ((n+1)th.MO), E_{Ll}. The excitation potential, E_P is a measure of energy required by an electron to jump from the HOMO to the LUMO. It may be related to the ease of carbonium ion formation in a compound. E_P values for various MePs are also included in Table 3. The values of E_{Hl} and E_P suggest that 4-MeP is the most reactive among all methyl derivatives of phenanthrene. It is followed by 1-,

TABLE 2—SUMMARY OF PREDICTED METABOLITES OF METHYLPHENANTHRENES

Molecule	Most probable metabolite (ultimate metabolite)	2nd. probable metabolite	3rd. probable metabolite
1-MeP	1,2-Diol-3,4-epoxide	7,8-Diol-5,6-epoxide 5,6-Diol-7,8-epoxide	9,10-Oxide
2-MeP	1,2-Diol-3,4-epoxide	7,8-Diol-5,6-epoxide 5,6-Diol-7,8-epoxide	9,10-Oxide
3-MeP	1,2-Diol-3,4-epoxide	7,8-Diol-5,6-epoxide 5,6-Diol-7,8-epoxide	9,10-Oxide
4-MeP	1,2-Diol-3,4-epoxide	7,8-Diol-5,6-epoxide 5,6-Diol-7,8-epoxide	9,10-Oxide
9 MeP	1,2-Diol-3,4-epoxide 3,4-Diol-1,2-epoxide	7,8-Diol-5,6-epoxide 5,6-Diol-7,8-epoxide	9,10-Oxide

TABLE 3—CHARACTERISTIC MOLECULAR PROPERTIES* OF METHYLPHENANTHRENES

Location of methyl group	D_{CM}	$-E_{CM}$	$-E_{H_1}$	E_{L_1}	E_P
1	1.508	15.365	7.832	0.181	8.018
2	1.506	15.367	7.900	0.204	8.104
3	1.504	15.404	7.854	0.184	3.088
4	1.524	14.491	7.799	0.232	8.031
5	1.513	15.079	7.773	0.200	7.973
6	1.504	15.491	7.843	0.186	8.029
7	1.503	15.425	7.865	0.237	8.102
8	1.504	15.474	7.862	0.212	8.074
9	1.508	15.357	7.831	0.186	8.017
10	1.509	15.379	7.821	0.165	7.986

*Except for D_{CM} which is in Å all other molecular quantities are in eV.

and 9-MePs. The prediction by E_{L_1} is little different, according to which 2-, and 9-MePs followed by 4-MeP are the most reactive. E_{H_1} is, in fact, equivalent to the first ionization potential, and E_{L_1} to the electron affinity of MePs. The lower the ionization potential, the greater is the chance of carbonium ion formation in a compound. Similarly, the higher the electron affinity, the more electrophilic is the compound, and greater is the probability of interaction between carcinogen and DNA. Due to steric hindrance from a methyl group at position 4 the metabolite which is formed in the region is likely to get detoxified. In phenanthrene (Fig. 1) 1, 2, 3, and 4 positions which are equivalent to 8, 7, 6 and 5 positions, respectively also form part of the same bay. 4-Methyl group is at peri position with respect to the second bay-region terminal ring. It, therefore, appears that 4-MeP can be the most reactive in case the metabolite is formed in the second terminal ring. The first and second columns of Table 3 list the distance D_{CM}, between the methyl carbon and the backbone carbon directly attached to the methyl group, and the total two center electronic energy E_{CM}, between the same carbon atoms, respectively. High positive value of D_{CM} and least negative value of E_{CM} reaffirm that 4-MeP is the most carcinogenic in the series. Availability of quantitative data from high precision experiment justifies validity of the above predictions.

Conclusion :

The results reported in the present article lend strong supports to the idea that electronic parameters determined by quantum mechanical method are able to elucidate carcinogenic properties of MePs. To our knowledge, no experimental results are available to provide comparison with predicted metabolic products. Yang *et al.*[25] undertook studies of the metabolism of twelve MBAs, with rat liver microsomes. They observed that with the exception of 3-MBA, the proximate metabolite for all other eleven MBAs was 3,4-diol. The metabolite is identical to that of BA. In the case of phenanthrene the proximate metabolite is 1,2-diol. On the basis of observations for MBAs that contrary to usual generalization[26,27], microsomal enzymes may epoxidize the aromatic double bond with a methyl substituent, and the epoxides may be subsequently hydrated to dihydrodiols by the microsomal epoxide hydrase, the proximate metabolite of MePs should also be 1,2-diol. In case it is true, the predicted metabolites would be in quantitative agreement with the experiments.

Acknowledgement

The author is grateful to the C.S.I.R., New Delhi for supporting the project, and to Prof. D. Nasipuri and Prof. H. N. Bose for their interests in the present work.

References

1. E. J. BAUM in "Polycyclic Hydrocarbons and Cancer", eds. H. V. GELBOIN and P. O. P. Ts'o, Academic Press, New York, 1978, Vol. 1, p. 45.
2. C. E. SEARLE, "Chemical Carcinogens", A. C. S. Monograph, 1976, p. 173.
3. D. H. PHILLIPS and P. SIMS in "Chemical Carcinogens and DMA", ed. P. L. GROVER, C. R. C. Press, Boca Raton, 1977, Vol. 2, p 29.
4. J. A. MILLER, *Cancer Res.*, 1970, **30**, 559.
5. P. G. WISLOCKI, K. M. FIORENTINI, P. P. FU, S. K. YANG and A. Y. H. LU, *Carcinogenesis*, 1982, 3, 215.
6. J. C. BARRETT and P. O. P. Ts'o, in "Polycyclic Hydrocarbons and Cancer", eds. H. V. GELBOIN and P. O. P. Ts'o, Academic Press, New York, 1978, Vol. 2, p. 43.
7. C. C. HARRIS, V. M. GENTA, A. L. FRANK, D. G. KAUFFMANN, L. A. BARRETT, E. M. MCDOWALL and B. F. TRUMP, *Nature* (*London*), 1974, **252**, 68.
8. J. BOOTH, G. R. KEYSELL, K. PAL and P. SIMS, *FEBS Lett.*, 1974, **43**, 341.
9. P. SIMS in "Screening Tests in Chemical Carcinogenesis", eds. R. MONTESANO, H. BARTSCH and L. TOMATIS, International Agency for Research on Cancer, Lyon, 1974, p. 211.

10. R. P. IYER, J. W. LYGA, J. A. SECREST III, G. H. DAUB and T. J. SLAGA, *Cancer Res.*, 1980, **40**, 1073.
11. E. J. LAVOIE, L. TULLEY-FREILEV, V. BEDENKO and D. HOFFMANN, *Cancer Res.*, 1981, **41**, 3441.
12. E. J. LAVOIE, V. BEDENKO, N. HIROTO, S. S. HECHT and D. HOFFMANN in "Polycyclic Aromatic Hydrocarbons", eds. P. W. JONES and P. LEBER, Ann Arbor Science Publishers, Ann Arbor, 1969, p. 505.
13. S. S. HECHT, W. E. BONDINELL and D. HOFFMANN, *J. Natl. Cancer Inst.*, 1974, **52**, 1121.
14. S. S. HECHT, M. LOY, P. R. MARONPOT and D. HOFFMANN, *Cancer Lett.*, 1976, **1**, 147.
15. S. NOOR MOHAMMAD, *Indian J. Chem., Sect. A*, 1983, **22**, 639 ; *Indian J. Biochem. Biophys.*, in the press.
16. S. NOOR MOHAMMAD, *Indian J. Biochem. Biophys.*, in the press.
17. S. NOOR MOHAMMAD in "Polynuclear Aromatic Hydrocarbons", eds. M. COOKE and A. J. DENNIS, Battelle Press, Columbus, 1984, in the press.
18. S. NOOR MOHAMMAD, *J. Theoret. Biol.*, submitted.
19. S. NOOR MOHAMMAD, *Indian J. Biochem. Biophys.*, in the press.
20. S. NOOR MOHAMMAD, *Brit. J. Cancer*, unpublished.
21. R. C. BINGHAM, M. J. S. DEWAR and D. H. LO, *J. Am. Chem. Soc.*, 1975, **97**, 1285.
22. R. FLETCHER and M. J. D. POWELL, *Comput. J.*, 1963, **6**, 163.
23. W. C. DAVIDON, *Comput. J.*, 1966, **10**, 406.
24. A. PULLMAN and B. PULLMAN, *Adv. Cancer Res.*, 1955, **3**, 117.
25. S. K. YANG, M. W. CHOU and P. P. FU in "Polynuclear Aromatic Hydrocarbons", eds. M. COOK and A. J. DENNIS, Battelle Press, Columbus, 1981, p. 253.
26. D. M. JERINA and J. W. DALY in "Drug Metabolism-From Microbe To Man", eds. D. V. PARKE and R. L. SMITH, Taylor and Francis Ltd., London, 1977, p. 13.
27. J. W. DALY, D. M. JERINA and B. WITKOP, *Experientia*, 1972, **28**, 1129.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 973-974

Search for New Fungicides. Part-I. Synthesis and Mercuration of Some New 2-Thio-Δ^4-thiazolines and Their Possible Use as Fungicides and Bactericides

(Mrs.) JUTHIKA MOHANTY and G. N. MAHAPATRA*

Department of Chemistry, Ravenshaw College, Cuttack-753 003

A series of new 2-thio-3-p-ethoxyphenyl-4,5-disubstituted-Δ^4-thiazolines (I) have been synthesised by condensing ammonium p-ethoxyphenyldithiocarbamate with a number of ketones in the presence of bromine in an alcoholic medium. The thiazolines have been mercurated with one equivalent of mercuric acetate in acetic acid medium. All the compounds have been assayed against the fungus *Pyricularia orysae* (Cav) and the bacteria *E. coli* and *S. aureus*.

RECENT use of 2-thio-thiazolines as antifungal[1] agents prompted us to synthesise new 2-thio-thiazolines with the hope of finding out potent fungicides. The present paper deals with the synthesis of twelve 2-thio-3-*p*-ethoxyphenyl-Δ^4-thiazolines (I) by condensing different ketones with ammonium *p*-ethoxyphenyldithiocarbamate in the presence of bromine in an alcoholic medium. The structure I has been confirmed through its unequivocal synthesis. 2-*p*-Ethoxyphenylimino-3-*p*-ethoxyphenyl-4-phenyl thiazoline (II ; $R_1=C_6H_5$, $R_2=H$) prepared by the condensation of sym-di-*p*-ethoxyphenylthiourea and acetophenone in the presence of bromine, on acid hydrolysis gives 2-oxo-3-*p*-ethoxyphenyl-4-phenyl-Δ^4-thiazoline (III ; $R_1=C_6H_5$, $R_2=H$) which on treatment with P_2S_5 in dry benzene gives I ($R_1=C_6H_5$, $R_2=H$).

When compound I is treated with mercuric acetate, it gives the monoacetoxy mercuric compound in which the acetoxy mercuric group enters into the *ortho*-position of the aryl nucleus attached to the N_3-position of the thiazoline moiety as the *para*-position is already occupied and never goes to the C_4-aryl nucleus[2,3].

Experimental

Ammonium p-*ethoxyphenyldithiocarbamate* : To a mixture of *p*-phenetidine (52 ml) and carbon disulphide (20 ml) in rectified spirit (40 ml) kept in ice bath, concentrated ammonia (41 ml) was added slowly. The mixture was stirred vigorously with a mechanical stirrer till a clear solution was obtained. The temperature was not allowed to rise above 30°. The dithiocarbamate was precipitated out, filtered and washed with ether and air dried (70%), m.p. 148° (Found : S, 27.74. $C_9H_{14}N_2S_2O$ requires S, 27.82%).

*2-Thio-3-*p*-ethoxyphenyl-4-phenyl-Δ^4-thiazoline* (I ; $R_1=C_6H_5$, $R_2=H$) : To acetophenone (2.4 g) in absolute alcohol (15 ml), bromine (4 g) dissolved in absolute alcohol (45 ml) was gradually added. Ammonium *p*-ethoxyphenyldithiocarbamate (5 g) was then added and refluxed for 18 h on a steam bath. Excess of alcohol was distilled off and residue was subjected to steam distillation to remove any excess of haloketone. The product was then treated with concentrated ammonia and the free base, thus obtained, was crystallised from ethanol to yield the product (70%), m.p. 140° (Found : S, 20.32.

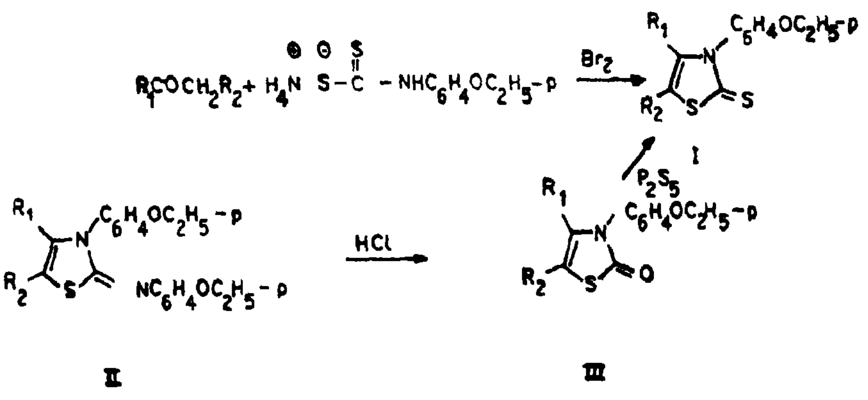


TABLE 1

Sl. no.	R_1	R_2	Thiazolines (I)* M.p. °C	Dilution for 50% germination of fungus	Inhibitory growth of bacteria in ppm *E. coli*	*S. aureus*	Mercuric derivatives of I** M.p. °C	Dilution for 50% germination of fungus	Inhibitory growth of bacteria in ppm *E. coli*	*S. aureus*
1.	C_6H_5	H	140	11.2	250	500	210	5	50	100
2.	CH_3	H	162	11.0	500	500	218	6	100	100
3.	p-$HO-C_6H_4$	H	185	9.0	500	500	228	3	50	50
4.	p-$Cl-C_6H_4$	H	148	7.0	100	250	>250	3	25	50
5.	p-$H_3C-C_6H_4$	H	120	11.3	500	250	>250	4	100	100
6.	p-$O_2N-C_6H_4$	H	210	10.0	250	250	>250	3	50	50
7.	p-$H_3CO-C_6H_4$	H	144	11.0	500	500	>250	5	100	100
8.	$C_6H_4-CH_2-CH_3$	H	201	10.2	250	250	>250	4	50	50
9.	CH_3	C_6H_5	125	10.8	500	500	195	5	100	100
10.	CH_3	CH_3	136	10.8	500	250	190	5	100	100
11.	α-$C_{10}H_7$	H	288	7.2	250	250	>250	5	50	100
12.	β-$C_{10}H_7$	H	165	8.0	250	250	245	3	50	100

* Elemental analysis (S) were within ±0.5% of the theoretical value.
** Elemental analysis (Hg) were within ±0.5% of the theoretical value.

$C_{17}H_{15}NS_2O$ requires S, 20.44%) ; IR : ν_{max}(KBr) 1489 (NCS), 1120 (CS) cm^{-1}.

2-Thio-3-o-acetoxymercuric-p-ethoxyphenyl-4-phenyl-Δ^4-thiazoline : I ($R_1=C_6H_5$, $R_2=H$; 1.2 g) dissolved in minimum quantity of acetic acid-ethanol (1 : 1, v/v) was added to a solution of mercuric acetate (1.0 g) dissolved in minimum volume of water-ethanol with constant stirring. The resulting solution was kept overnight at room temperature. The solid, thus obtained, was washed with hot water followed by ethanol and very dilute acetic acid to yield the product (65%), m.p. 210° (Found : Hg, 34.85. $C_{19}H_{17}NSO_3Hg$ requires Hg, 35.04%).

Antifungal activity : For fungicidal assay the method of Montgomery and Moore[4] taking *Pyricularia oryzae* (Cav), the causative organism of rice blast as the test fungus was used. The fungicidal assay (based on dilution necessary for 50% germination) is given in the Table 1. The spores were allowed to be kept in contact with fungicide at different concentrations for 24 h and percentage of germination was studied in that dilution. From the result of the fungicidal tests, it is found that although sulphur itself has fungicidal activity, introduction of sulphur at C_2-position does not contribute towards fungitoxicity. The presence of chlorine and naphthyl group in I increases the activity. Introduction of acetoxymercuric group markedly enhances the fungicidal activity.

Antibacterial activity : For bactericidal test, Rideal-Walker serial drop dilution method[5] taking gram-positive *S. aureus* and gram-negative *E. coli* as test bacteria was used. From the result of bactericidal test it is found that they show higher activity against *E. coli* than against *S. aureus*. Complete inhibition of bacterial growth occurs between 250-500 ppm. The mercurated derivatives are found to be more active, complete inhibition of bacterial growth occurs between 50-100 ppm.

Acknowledgement

We are thankful to B.S.I.R., Orissa for a research grant to carry out this work.

References

1. E. ALIMORE and S. I. ISKANDAROV, *Chem. Abstr.*, 1978, **88**, 89572.
2. G. N. MAHAPATRA and M. K. ROUT, *J. Indian Chem. Soc.*, 1955, **32**, 715.
3. G. N. MAHAPATRA, *J. Inst. Chem.*, 1956, **28**, 55.
4. H. B. S. MONTGOMERY and M. H. MOORE, *J. Pomol. Hort. Sc.*, 1938, **15**, 253.
5. S. RIDEAL and J. F. A. WALKER, *J. R. Sanit. Inst. London*, 1903, **24**, 424.

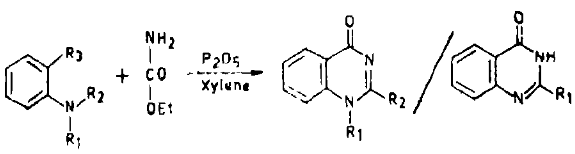
J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 975-978

Aminocarbonylation with Ethyl Carbamate : An access to Nitrogen Heterocycles†

D. P. CHAKRABORTY*, SWAPAN KUMAR ROY, U. P. JANA and T. KARMAKAR

Bose Institute, Calcutta-700 009

IN course of synthesis of some quinazolones (**1**, **2**, **3**) of Rutaceae [1,2] by the reaction of appropriately substituted anilides (**4**, **5**, **6**) with ethylacarbamate (**7**) in boiling xylene in presence of P_2O_5, our attention was drawn to the synthesis of quinazolones appropriate benzamide derivatives by Meyer and Wagner[3] as well as by Chakraborty *et al*[4]. Further, Gattermann[5] in 1888 showed that polar

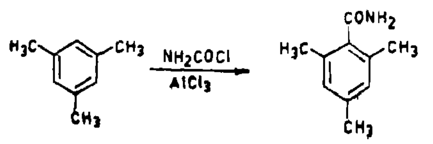


4 R_1=H, 7
R_2=COCH$_2$Ph,
R_3=H

1 R_1=CH$_2$Ph,
2 R_1=CH$_3$, R_2=CH$_2$Ph
3 R_1=CH$_3$,R_2=H

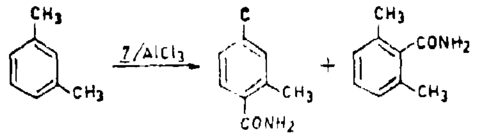
4a R_1=H, R_2=COCH$_2$Ph, R_3=CONH$_2$
5 R_1=CH$_3$, R_2=COCH$_2$Ph, R_3=H
5a R_1=CH$_3$, R_2=COCH$_2$Ph, R_3=CONH$_2$
6 R_1=CH$_3$, R_2=CHO, R_3=H

aromatic substrates like mesitylene (**9**) could be amidated to **10** with carbamyl chloride under Friedel-Crafts coditions.

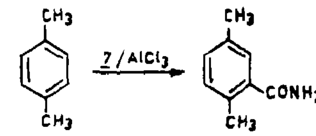


(9) (10)

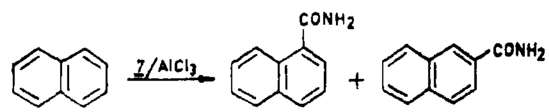
In consideration of the above facts, previously we showed[6] that appropriate anilides (**4**, **5**, **6**) could be C-aminocarbomylated at *ortho*-position (**4a**, **5a**, **6a**) with ethylcarbamate (**7**) under $AlCl_3$ catalysed condition. This could be cyclised to quinazolone with P_2O_5. In course of this reaction, we further showed that under Friedel-Craft's condition polar aromatic substrates (**9**, **11-13**) could be C-aminocarbonylated to the corresponding amides (**8**, **10**, **14-16**). Evidently our method provides a convenient modification of Gattermann's amidation reaction.



(11) (14) (8)

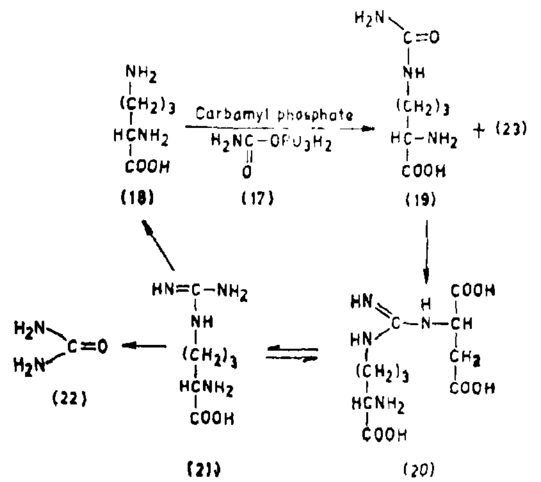


(12) (15)



(13) (16) (16a)

The aminocarbonylation involving the transfer of carbamyl group ($CONH_2$) from phosphate ester of carbamic acid (**17**) is a well known biochemical process by which one of the amino acids of the urea cycle, L-ornithin (**18**), is aminocarbomylated under enzyme mediation (*ornithin trans carbamylase*).

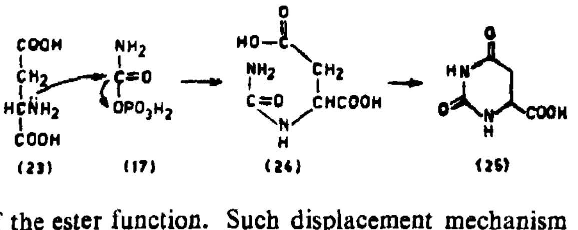


Through other two steps as shown above, the ornithin is regenerated. On the other hand, the

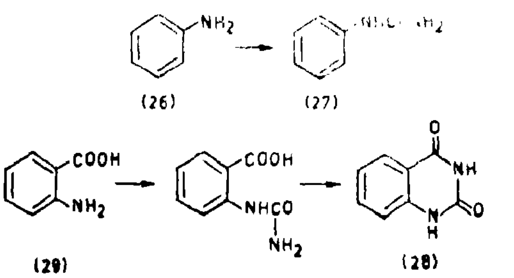
† Partly presented at Convention of Chemists held under auspices of Indian Chemical Society, Madras, 26-31 December, 1981.

biological carbamyl phosphate transfer with the phosphate ester of carbamic acid results in the *N*-aminocarbomylation of aspartic acid[8] (**23**). The carboamylated aspartic acid (**24**) under enzyme mediation gives rise to dihydroorotic acid (**25**), the key intermediate in the biosynthesis of pyrimidine nucleotides.

The overall mechanistic process in such enzyme mediated C–N bond formation involves the nucleophilic attack of the aminonitrogen on the carbon of the carbamyl phosphate and subsequent elimination



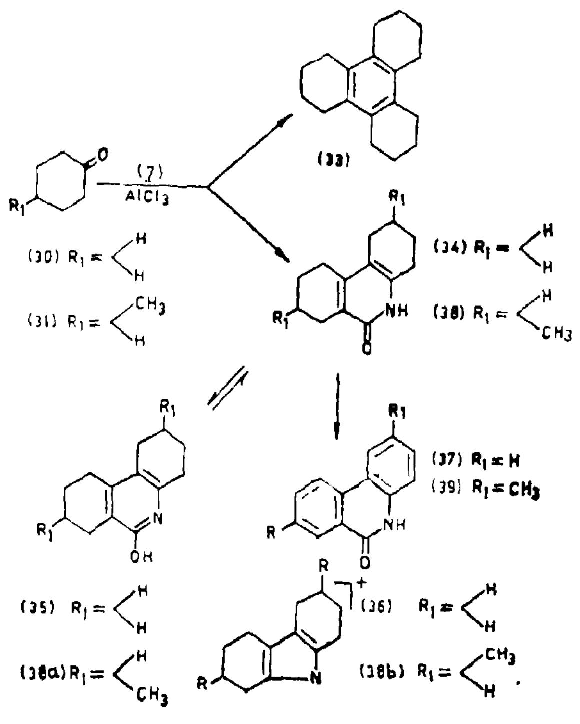
of the ester function. Such displacement mechanism has also been envisaged[9] in the reactions of higher alcohols with **7**. The nucleophilic attack of the aminonitrogen on the carbon of the ethylcarbamate (**7**) has been demonstrated by us during the formation of phenyl urea (**27**) from aniline (**26**) under Friedel-Crafts' condition as well as the formation of quinazolinedione (**28**) from anthranilic acid.



The synthesis of pyrimidine and of quinazolones *via* aminocarbonylation of different substrates with esters of carbamic acid, by nucleophilic attack on the carbon of the carbamic acid, prompted us to undertake further studies on C-aminocarbomylation with cyclohexanone, as they provide an appropriate nucleophile under the reaction conditions. In the present communication, we report our results on C-aminocarbonylation with cyclohexanone (**30**), 4-methyl cyclohexanone (**31**) and 2-methyl cyclohexanone (**32**) with (**7**) under Friedel-Crafts' condition.

Cyclohexanone (**30**) and ethyl carbamate (**7**) in a mixture of benzene and petroleum ether (b.p. 120-60°) on heating for six hours in presence of $AlCl_3$ furnished compounds 33 and **34**. The compound (**33**) $C_{18}H_{24}$ (M^+240) m.p. 231-32°, showed λ_{max} at 229 and 269 nm with log ε 4.12 and 2.45, and ν_{max} at 1652, 1580 and 1440 cm^{-1}. The mass spectral peak at *m/z* 77, of **33** could be reconciled with the presence of a phenyl ring in it. From all these data, **33** was characterised as *S*-dodecahydrotriphenylene[18] previously obtained by reacting cyclohexanone with concentrated HCl, H_2SO_4 or Lewis acids, like $ZnCl_2$ though its formation by boiling in presence of $AlCl_3$ has not been reported.

The compound **34**, $C_{13}H_{17}NO$ (M^+203), m.p. 290°, was insoluble in dilute HCl but soluble in concentrated H_2SO_4 and gave a red colouration with $FeCl_3$ solution. The uv spectrum of this compound at λ_{max} 231 and 301 nm with log 4.57 and 4.68 like pyridone[10] (λ_{max} 224 and 293 nm with ε 7230 and 5900, respectively, vapour phase[11] λ_{max} 295 nm) and *N*-methyl pyridone (λ_{max} 226 and 297 with ε 6100 and 5700, together with ir band at ν_{max} 1630-40 (NH), 1550 and 1270 cm^{-1} (C–N and NH) support the presence of pyridone fragment in **34**. The absence of band at 3300 cm^{-1} region does not show the absence of a pyridone system, for which the band at 1650 cm^{-1} region is more characteristic[12]. The nmr data of **34** showed signals at δ 11.9 (1H, CO–NH) 2.5-2.7 (4H, m, benzylic protons), 2.3-2.5 (4H, m, benzylic protons) and 1.65-1.95 (8H, aliphatic protons). The highly deshielded signal at δ 11.9 could be attributed to the NH proton of the α-pyridone system. This could be explained due to facile

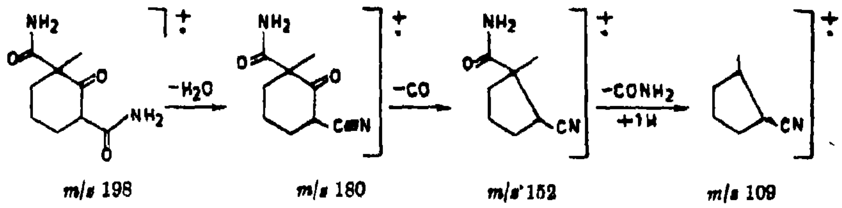


lactam-lactim (**34**-**35**) tautomerism. The mass spectral data showed the peak at *m/z* 203. The significant peak at *m/z* 174 (M-28-1) could be presented by **36** similar to those recorded in case of phenanthididones.

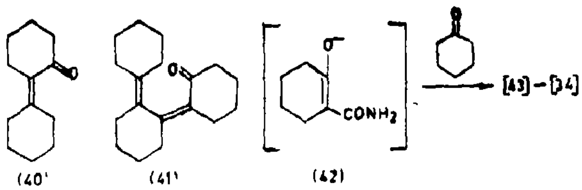
^{13}C nmr spectrum of the compound with signals at δ 215.14 (C=O) and 163.5 (C attached to the nitrogen) also support the proposed structure **34** for the nitrogenous product. This has been confirmed by dehydrogenation of **34** to phenanthridone (**37**), m.p. 293°. 4-Methylcyclohexanone (**31**)

under above experimental conditions furnished a nitrogenous compound, $C_{15}H_{21}NO$ (**38**) (M^+231). The positive $FeCl_3$ reaction and the uv spectrum, λ_{max} 230 and 303 with log ε 4.7 and 4.3 were suggestive of the pyridone structure like **34**. This has also been supported by its ir spectrum, ν_{max} 1625-35, 1550 and 1275 cm^{-1}. The pmr data of **38** showed signal at δ12.1 (**38a** ; 1H, lactam-lactim tautomer) and 2.30-3.13 (m, 8H, benzylic proton), 1.6-2.25 (m, 6H, 4-methylene protons together with 2-methine protons). Like **34** its mass spectral data show significant peak at *m/z* 201 which could be represented by **38b**. The dehydrogenation of **38** to 5,9-dimethylphenanthridone (**39**) confirmed the structure of **38**.

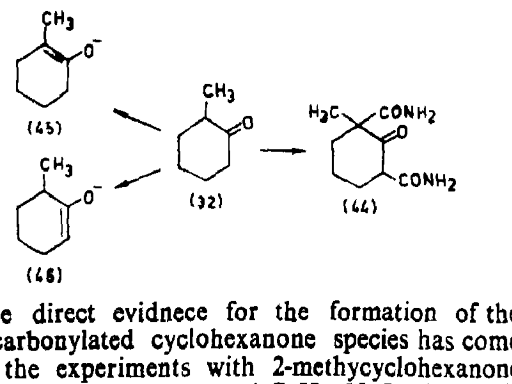
of amide system and six-membered ketone. One of the amide nitrogen is chelated (ν_{max} 3050 cm^{-1}). The pmr data showed bands for NH protons at δ 7.85 and 7.6 (2H), while the other signal was at 5.23 (2H, broad). 2-Methylcyclohexanone gives rise to two enolate ions[16], **45**, **46** of which **45** is preferentially attacked giving rise to the intermediate monoamide after which amidation of the second enolate takes place resulting into **44**. The situation is very similar to the alkylation of unsymmetrical ketones resulting into isomeric products. This amide perhaps cannot react further to yield pyridone derivatives due to stereoelectronic factors. The structure **44** was also supported by its mass spectral fragmentation.



The formation of *S*-dodecahydrotriphenylene by acid catalysis is considered to be an aldol type reaction of cyclothexanone wherein one molecule attacks the reactive methylene of the other. The idea has been substantiated by the isolation of the species (**40**, **41**)[13].



Evidently the $AlCl_3$ catalysed enolised[14] species could be assumed to be C-aminocarbolylated to **42** which reacts with another molecule of cyclohexanone to give the intermediate **43** which readily gives rise to the stabler species **34**. Such ready transformation to a stabler species is remimiscent of the enamine chemistry[15].



The direct evidnece for the formation of the amnocarbonylated cyclohexanone species has come from the experiments with 2-methycyclohexanone when nitrogenous compound $C_9H_{14}N_2O_3$ (M^+198), λ_{max} 250 nm (log ε 4.12) (**44**) was isolated. The ir spectrum of the compound showed bands at 3150, 3050, 1720 and 1656 cm^{-1} showing the presence

Above experiments show that under appropriate conditions cyclohexanones may be aminocarboylated and in some cases transient amide immediately reacts to yield the heterocyclic system.

From the data and discussions it is evident that aminocarbonylation with esters of carbamic acid appears to be a convenient method for *N*-heterocyclisation whereby an additional nitrogen is inserted from the carbamyl group. Aminocarbonylation by ethylcarbamate provides a laboratory analogy of biological aminocarbonylation with carbamyl phosphate.

Experimental

All melting points are uncorrected. Analytical samples were analysed after drying over P_2O_5 *in vacuo* at 80° for 24 h.

Attempted aminocarbonylation of cyclohexanone with ethyl carbamate :

Preparation of octahydro phenanthridone (**34**) : A mixture of cyclohexanone (0.3 mol) and ethylcarbamate (0.3 mol) in dry benzene was diluted with petroleum ether to 50 ml. To the reaction mixture anhydrous $AlCl_3$ (0.33 mol) was added portionwise in cold. After careful shaking the reaction mixture was refluxed for 5 h, cooled, acidified with cold dilute HCl and neutralized with $NaHCO_3$. The solution was extracted with ethyl acetate (3×150 ml). After making the solution acid-free and dry, the solvent was removed when an oily mass was obtained from which crystals were obtained after cooling. The crystals obtained after filtration melted at 231-32° after crystallisation from a mixture of benzene and petroleum ether (b.p. 60-80°)(18%, lit.[13] highest yield 13%). This was characterised as *S*-dodecahydrotriphenylene,

$C_{18}H_{24}$ (lit. m.p. 230°) (Found : C, 90.20 ; H, 10.0. $C_{18}H_{24}$ requires C, 90.0 ; H, 10.0%).

The oily liquid after dilution with chloroform (35 ml) yielded yellowish crystals, which on recrystallisation from ethanol furnished a homogenous nitrogenous compound (70%), m.p. 292-3° (Found : C, 76.79 ; H 8.22 ; N, 6.70. $C_{13}H_{17}NO$ requires C, 76.8 ; H, 8.37 ; N, 6.89%) ; ^{13}C nmr 215.14, 163.55, 148.78, 138.01, 118.44, 78.50, 26.78, 26.19, 23.24, 22.61, 22.12, 21.75 and 21.54.

Dehydrogenation of octahydrophenanthridone to phenanthridone (**37**) : Octahydrophenanthridone (30 mg) mixed with catalytic amounts of Pd/C in *p*-cymene (2.5 ml). The mixture was heated in a sealed tube at 220° for 5 h. The mixture diluted with chloroform, filtered. The filtrate on concentration gave a colourless solid which on crystallisation from benzene furnished homogenous colourless crystals of phenathridone, m.p. 293° (lit. m.p. 293°); ν_{max} 3400, 1670, 1640, 1615, 1560 cm^{-1} ; λ_{max} 224, 230, 236.5, 258, 269, 308, 321, 335.5 nm with log ϵ 5.05, 5.22, 5.03, 4.12, 4.25, 3.99, 3.81, 3.86, 3.81.

Synthesis of 5,9-dimethyl-octahydrophenanthridone (**38**) : A mixture of 4-methylcyclohexanone (0.3 mol) and ethyl carbamate (0.3 mol) in minimum quantity of benzene was diluted to 50 ml by adding high boiling petroleum ether (b.p. 120-60°). $AlCl_3$ (0.33 mol) was added in portion and the mixture was refluxed at 170-190° for 6 h. Working up of the reaction products gave an oily mass from which colourless crystals of 5,9-dimethyloctahydrophenanthridone (**36**) was obtained after repeated crystallisation from a mixture of benzene and petroleum ether, (70%), m.p. 260° (Found: C, 77.95 ; H, 9.09; N, 6.08. $C_{15}H_{21}NO$ requires C, 77.92 ; H, 9.12 ; N, 6.06%) ; ν_{max} 1625-35 and 1550 cm^{-1} ; δ 12.1 (1H), 2.30-2.25 (8H), 1.16 (6H), 1.16 (3H) and 1.08 (3H) ; *m/z* 231 (M^+), 230 (69%), 216, 202 and 201.

Dehydrogenation of 5,9-dimethyloctahydrophenanthridone to 5,9-dimethylphenanthridone (**39**) : 5,9-Dimethyl-octahydrophenanthridone (50 mg) was mixed with catalytic amounts of Pd/C and a few drops of *p*-cymene added. The reaction mixture was then heated at 220° for 15 h in a sealed tube. Working up of the reaction mixture give a homogenous compound which was characterised as 5,9-dimethylphenanthridone m.p. 256° (lit. m.p. 256°) (Found : C, 80.74 ; H, 5.80 ; N, 6.30. $C_{15}H_{13}NO$ requires C, 80.71 ; H, 5.82 ; N, 6.27%).

Amino carbomylation of 2-methyl cyclohexanone with ethylcarbamate, formation of **44** : To a solution of 2-methylcyclohexanone (0.3 mol) and ethyl carbamate (0.3 mol) in dry benzene and high boiling petroleum ether (45 ml). $AlCl_3$ (0.33 mol) was added in portions and the reaction mixture was refluxed for 10 h at 200-210° (bath temp.). After work up as above a colourless solid was obtained after repeated crystallisation from a mixture of benzene and petroleum ether (62%), m.p. 216-17° (Found : C, 54.76 ; H, 7.24 ; N, 14.32. $C_9H_{14}N_2O_3$ requires C, 54.54 ; H, 7.07 ; N, 14.14%) ; ν_{max} 3150, 3050, 1720 and 1665 cm^{-1} ; λ_{max} 250 nm with log ϵ 4.12; δ 7.85, 7.6 ($CONH_2$), 5.25 ($CONH_2$), 1.88-2.33, 1.47 (3H); *m/z* 198 (M^+), M-18 (100%), 65, 152, 137, 126, 109 and 94.

Acknowledgement

The authors wish to thank Dr. S. C. Bhattacharyya, Director, and Dr. A. K. Barua, Head of the Department, Bose Institute for their interest in the work. Two of the authors (U.P.J. and T.K.) gratefully acknowledge the financial support by C.S.I.R., New Delhi.

References

1. M. Sarkar, D. P. Chakraborty, *Phytochemistry*, 1979, **18**, 694 ; 1977, **16**, 2007.
2. P. Bhattacharyya, M. Sarkar, T. Roy Chowdhury and D. P. Chakraborty, *Chem. Ind.* (*London*), 1978, 532.
3. J. E. Meyer and E. C. Wagner, *J. Org. Chem.*, 1948, **8**, 239.
4. D. Chakraborty, R. N. Chakraborty and S. C. Chakraborty, *J. Chem. Soc.*, 1958, 3337.
5. L. Gattermann, *Justus Liebigs Ann. Chem.*, 1888, **56**, 244.
6. D. P. Chakraborty, A. K. Mandal and S. K. Roy, *Synthesis*, 1981, 977.
7. E. E. Conn and P. K. Stumpf in "Outlines of Biochemistry", John Wiley, London, 1972, p. 386.
8. P. Reichand, *Adv. Enzymol.*, 1959, **21**, 263.
9. P. Adams and F. A. Baron, *Chem. Rev.*, 1965, **65**, 567.
10. A. I. Scott in "Interpretation of UV Spectra of Natural Products", Pergamon Press, 1964, p. 178.
11. J. Frank and A. R. Katrizky, *J. Chem. Soc.*, *Perkin Trans. 2*, 1976, 1428.
12. J. A. Gibson, W. Kynastin and A. S. Lindsay, *J. Chem. Soc.*, 1955, 4340.
13. C. M. Buess and D. D. Lawson, *Chem. Rev.*, 1960, **60**, 313.
14. H. O. House, V. Paragamian, R. S. Ro and D. J. Wluke, *J. Am. Chem. Soc.*, 1960, **82**, 1457.
15. J. Szmuszkoviez in "Advances in Organic Chemistry", Interscience, New York, 1963, p. 71.
16. E. C. Du Ienm, F. J. Maqrillin and R. Robinson, *J. Chem. Soc.*, 1937, 53.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 979-981

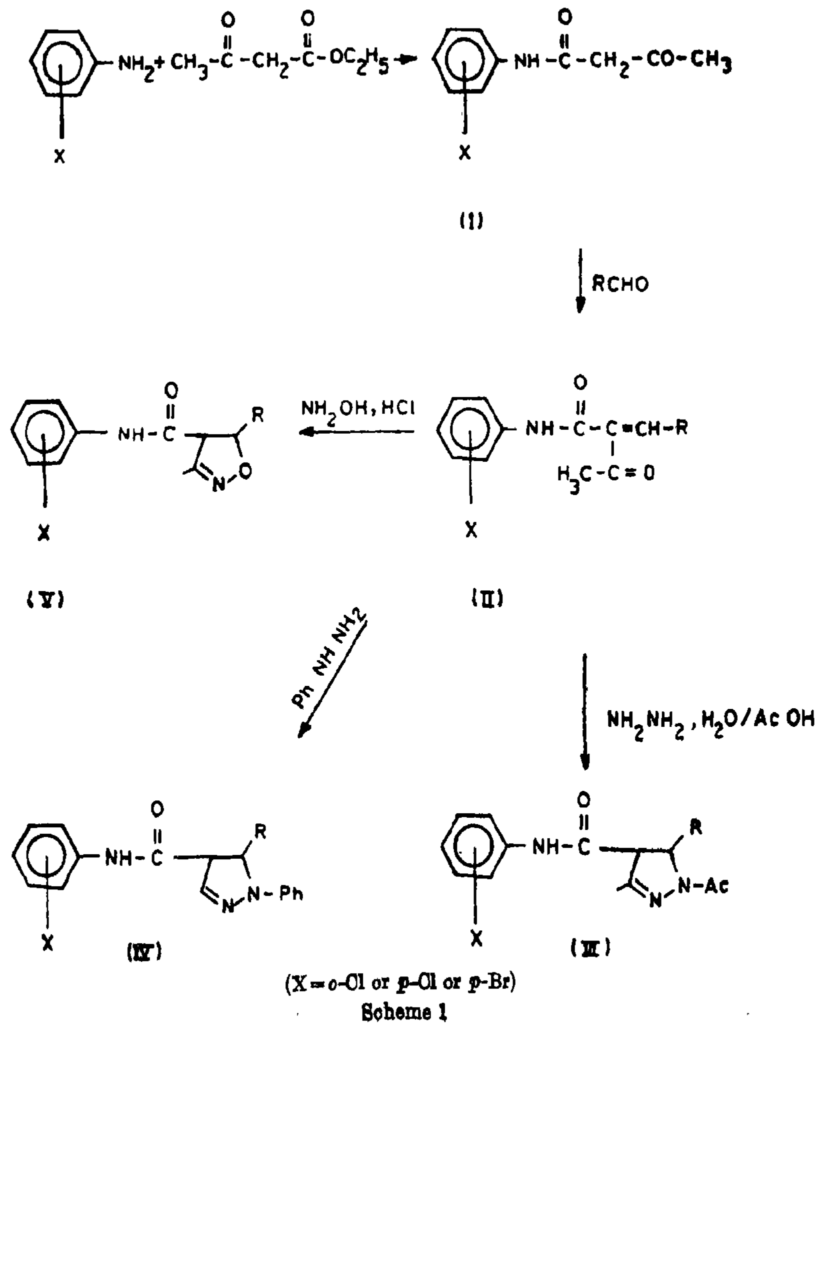
Synthesis and Biological Activity of Some Haloanilido Pyrazoline and Isoxazoline Derivatives

N. K. MANDAL, R. SINHA and K. P. BANERJEE*

P. G. Department of Chemistry, Bhagalpur University, Bhagalpur-812 007

Halogenoacetoacetanilide on condensation with aromatic aldehyde yielded the corresponding haloanilido α,β-unsaturated ketones which on heating with hydrazine hydrate/phenylhydrazine and hydroxylamine hydrochloride gave the corresponding haloanilido pyrazoline and isoxazoline derivatives. The biological activities of the compounds were evaluated.

A perusal of the literature[1-5] on pyrazolines and isoxazolines has revealed that these compounds are not only used in textile and cinematographic film industry but they also show widely differing biological activities as bactericides, insecticides, fungicides, anaesthetics, analgesics and antidiabetic agents. Amino compounds, in general, are well known for their manifold physiological actions. Again, the presence of halogen atoms in a compound is known to have an activity-enhancing effect. Considering all these factors, it was thought worthwhile to synthesise a few haloanilido pyrazoline and isoxazoline derivatives (Scheme 1) and to evaluate their biological action.



(X = o-Cl or p-Cl or p-Br)
Scheme 1

Experimental

All melting points are uncorrected. Ir spectra (KBr) were recorded on Beckman IR-20 spectrophotometer.

Aceto-o-chloroacetanilide (I) : A mixture of *o*-chloroaniline (0.01 mol) and ethylacetoacetate (0.01 mol) was heated to 130° for 1.5 h. On cooling, the colourless crystals of I were separated. It was filtered off and then recrystallised from ethanol to yield the product (65%), m.p. 102°.

3-(o-Chloroanilido)-4-aryl-but-3-en-2-one (II) : A mixture of (I ; 0.01 mol) and an aromatic aldehyde (0.01 mol) was fused for 0.25 h and the resulting mass was cooled and treated with petroleum ether (b.p. 60-80°). The product was filtered and crystallised from ethanol to yield II. The results are incorporated in Table 1.

TABLE 1—3-HALOANILIDO-4-ARYL-BUT-3-EN-2-ONE (II)

Compd. no.	X	R	M.p. °C	Colour	Yield %
IIa	o-Cl	p-NO$_2$-C$_6$H$_4$	159	Yellow	56
IIb	o-Cl	m-NO$_2$-C$_6$H$_4$	165	Yellow	52
IIc	o-Cl	3-OH-4-OCH$_3$-C$_6$H$_3$	144	Yellow	57
IId	p-Cl	p-NO$_2$-C$_6$H$_4$	164	Yellow	54
IIe	p-Cl	m-NO$_2$-C$_6$H$_4$	142	Brown	65
IIf	p-Cl	3-OH-4-OCH$_3$-C$_6$H$_3$	152	Yellow	69
IIg	p-Br	p-NO$_2$-C$_6$H$_4$	162	Yellow	67
IIh	p-Br	m-NO$_2$-C$_6$H$_4$	133	Yellow	85
IIi	p-Br	3-OH-4-OCH$_3$-C$_6$H$_3$	198	Yellow	70

All compounds gave satisfactory (C, H) elemental analyses.

N-*Acetyl-3-methyl-4-(o-chloroanilido)-5-arylpyrazolines* (III) : A mixture of *o*-chloroanilido-α,β-unsaturated ketone (II), hydrazinehydrate (0.015 mol), ethanol (30 ml) and glacial acetic acid (10 ml) was refluxed for 8 h. The resulting solution was concentrated, cooled and poured over ice-water when product III was separated which was filtered and crystallised from a mixture of ethanol-petroleum ether (1 : 1). The results are incorporated in Table 2.

TABLE 2—N-ACETYL-3-METHYL-4-HALOANILIDO-5-ARYL-PYRAZOLINE (III)

Compd. no.	X	R	M.p. °C	Colour	Yield %
IIIa	o-Cl	p-NO$_2$-C$_6$H$_4$	110	Red	72
IIIb	o-Cl	m-NO$_2$-C$_6$H$_4$	96	Red	65
IIIc	o-Cl	3-OH-4-OCH$_3$-C$_6$H$_3$	71	Red	59
IIId	p-Cl	p-NO$_2$-C$_6$H$_4$	141	Yellow	52
IIIe	p-Cl	m-NO$_2$-C$_6$H$_4$	187	Red	62
IIIf	p-Cl	3-OH-4-OCH$_3$-C$_6$H$_3$	216	Yellow	52
IIIg	p-Br	p-NO$_2$-C$_6$H$_4$	201	Red	85
IIIh	p-Br	m-NO$_2$-C$_6$H$_4$	176	Yellow	62
IIIi	p-Br	3-OH-4-OCH$_3$-C$_6$H$_3$	187	Yellow	71

All compounds gave satisfactory (C, H) elemental analyses.

N-*Phenyl-3-methyl-4-(o-chloroanilido)-5-arylpyrazolines* (IV) : A mixture of *o*-chloroanilido-α,β-unsaturated ketone (II), phenylhydrazine (0.01 mol), ethanol (30 ml) and piperidine (1 ml) was refluxed for 9 h. The resulting mixture was concentrated, cooled and then poured onto acidified ice-water. Coloured compounds were separated which were filtered and crystallised from ethanol-petroleum ether (1 : 3). The results are incorporated in Table 3.

TABLE 3—N-PHENYL-3-METHYL-4-HALOANILIDO-5-ARYL-PYRAZOLINE (IV)

Compd. no.	X	R	M.p. °C	Colour	Yield %
IVa	o-Cl	p-NO$_2$-C$_6$H$_4$	126	Red	75
IVb	o-Cl	m-NO$_2$-C$_6$H$_4$	97	Red	71
IVc	o-Cl	3-OH-4-OCH$_3$-C$_6$H$_3$	94	Red	65
IVd	p-Cl	p-NO$_2$-C$_6$H$_4$	98	Reddish brown	66
IVe	p-Cl	m-NO$_2$-C$_6$H$_4$	138	Reddish yellow	75
IVf	p-Cl	3-OH-4-OCH$_3$-C$_6$H$_3$	110	Red	72
IVg	p-Br	p-NO$_2$-C$_6$H$_4$	81	Yellow	81
IVh	p-Br	m-NO$_2$-C$_6$H$_4$	74	Reddish yellow	72
IVi	p-Br	3-OH-4-OCH$_3$-C$_6$H$_3$	66	Red	81

All compounds gave satisfactory (C, H) elemental analyses.

3-Methyl-4-(o-chloroanilido)-5-aryl-isoxazoline (V) : A mixture of *o*-chloroanilido-α,β-unsaturated ketone (II, 0.01 mol) hydroxylamine hydrochloride (0.015 mol), ethanol (30 ml) and KOH (0.015 mol) was refluxed for 10 h. The resulting mixture was concentrated, cooled and then poured onto ice-water. The compound V was filtered and crystallised with ethanol-petroleum ether (1 : 3). The results are incorporated in Table 4.

TABLE 4 – 3-METHYL-4-HALOANILIDO-5-ARYL-ISOXAZOLINE (V)

Compd. no.	X	R	M.p. °C	Colour	Yield %
Va	o-Cl	p-NO$_2$-C$_6$H$_4$	121	Red	64
Vb	o-Cl	m-NO$_2$-C$_6$H$_4$	102	Reddish yellow	62
Vc	o-Cl	3-OH-4-OCH$_3$-C$_6$H$_3$	95	Red	62
Vd	p-Cl	p-NO$_2$-C$_6$H$_4$	82	Red	61
Ve	p-Cl	m-NO$_2$-C$_6$H$_4$	185	Red	45
Vf	p-Cl	3-OH-4-OCH$_3$-C$_6$H$_3$	186	Reddish yellow	71
Vg	p-Br	p-NO$_2$-C$_6$H$_4$	110	Yellow	61
Vh	p-Br	m-NO$_2$-C$_6$H$_4$	110	Yellow	82
Vi	p-Br	3-OH-4-OCH$_3$-C$_6$H$_3$	183	Yellow	51

All compounds gave satisfactory (C, H) elemental analyses.

Biological screening of some pyrazoline derivatives:

Biological screening of some pyrazoline derivatives was done following the method of Verma and Nobles[6] and the results are recorded in Table 5.

Results and Discussion

The haloanilido-α,β-unsaturated ketones (II), prepared by the condensation of halogenoacetoacetanilide with aldehydes, showed absorption bands at 1690 (conjugated CO), 1600 (olefinic double bond)

TABLE 5—BIOLOGICAL SCREENING OF SOME HALOANILIDO PYRAZOLINES

Compd. no.	*B. Subtalis*	*E. Coli*	*Xanthromonus citri*	*B. pumilis*
IVa	++	–	+	–
IVb	–	–	–	++
IVc	–	–	++	–
IIIb	+	+	–	+
Tetracycline	+++	+++++	+++	+++

Inhibition zone size : + = 6 – 12, ++ = 12 - 18, +++ = 18 - 24, ++++ = 24 - 30, +++++ = > 30 mm. – = No inhibition.

and 3320 cm^{-1} (NH). Ketones (**II**), when heated with hydrazine and phenylhydrazine, the corresponding haloanilido pyrazolines **III** and **IV** were directly obtained, obviously, *via* the initial formation of hydrazone and phenylhydrazone derivatives which cyclise under the experimental conditions. The formation of these pyrazolines was confirmed by their positive Knorr's colour test[7] which is a characteristic test for aryl pyrazolines. The structures of **III** and **IV** were fully corroborated by ir spectral data which showed absorption at 1660 (C=O), 1600 (C=N), 3320 (NH) and 1230 cm^{-1} (C–N). Similarly, ketones (**II**), on heating with hydroxylamine hydrochloride yielded the correspond ing haloanilido isoxazolines (**V**), which showed ir absorption at 1600 (C=N), 1660 (C=O) and 3320 cm^{-1} (NH).

The biological activity of some representative compounds was initially tested and it was found that the compound **IVa** showed activity against *B. subtalis*, **IVc** against *Xanthromonus citri* and **IVb** against *B. pumilis*. The results of the screened compounds showed 66% inhibition effect towards some specific organisms, taking tetracycline as the standard (100%). It may be seen from Table 5 that *N*-phenylhaloanilido pyrazoline derivatives are more active than their corresponding *N*-acylhaloanilido counterparts and probably the position of the subs- tituent in aryl ring attached to pyrazoline nucleus may have some influence for exhibiting different activity on different organisms. The present screen- ing, however, does not permit to draw a general conclusion and work is in progress on these lines.

Acknowledgement

The authors wish to thank Dr. K. D. Banerji, Prof. and Head of the Department of Chemistry, Bhagalpur University for providing facilities.

References

1. G. F. DUFFIN and J. D. KENDALL, *J. Chem. Soc.*, 1954, 408.
2. M. STAMPER and B. F. AYCOCK, *J. Am. Chem. Soc.*, 1954, **76**, 2786.
3. A. M. OSMAN, KH. M. HASSAN and M. A. EL-MAGHRARY, *Indian J. Chem., Sect. B*, 1976, **14**, 282.
4. Z. H. KHALIL and A. S. YANNI, *J. Indian Chem. Soc.*, 1981, **58**, 168.
5. R. P. BARNES, G. E. PINKNEY and G. M. PHILLIPS, *J. Am. Chem. Soc.*, 1954, **76**, 276.
6. R. S. VARMA and W. L. NOBLES, *J. Pharm. Sci.*, 1968, **57**, 1801.
7. V. KNORR, *Ann.*, 1887, **238**, 200.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 982-984

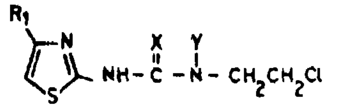
Heterocyclic Compounds. Part—IX† Syntheses of *N*-Nitrosoureas and *N*-Nitrosothioureas as Possible Antitumor Agents

J. SAHU, S. N. DEHURI, S. K. NAIK and A. NAYAK*

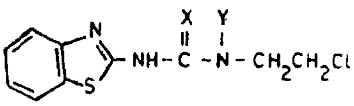
Department of Chemistry, Sambalpur University, Jyoti Vihar, Burla, Sambalpur-768 017

The synthesis of several novel *N*-nitrosoureas and *N*-nitrosothioureas from various heterocyclic and alicyclic amines have been described. Nitrosoureas were prepared by nitrosation of ureas using $NaNO_2$ in formic acid whereas nitrosothioureas were obtained by nitrosation of thioureas under slightly acidic condition. The higher acidic reaction condition of thioureas favoured nitrosation at more reactive sulphur leading to urea derivatives *via* thionitrosyl intermediate. The antitumor activity of some compounds has been evaluated against leukemia L1210.

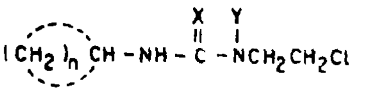
1-(β-Chloroethyl)-3-alkyl-1-nitrosoureas[1,2] (CENU's) and several related compounds[3,4] are clinically useful in the treatment of range of malignant diseases. The present study is directed towards the synthesis of several heterocyclic nitrosoureas and their sulphur analogues with a view to evaluating their antitumor activity. The sulphur analogues of the urea derivatives have been chosen because of the fact that the isothiocyanates themselves exhibit antitumor properties. 3-(4-Arylthiazolyl-2)-1-(2-chloroethyl)-1-nitrosoureas (I; X=O, Y=NO), 3-(benzothiazolyl-2)-1-(2-chloroethyl)-1-nitrosoureas (II; X=O, Y=NO), 3-(cycloalkyl)-1-(2-chloroethyl)-1-nitrosoureas (III; X=O, Y=NO, n=4-6) and bis(2-chloroethyl-1-nitrosourea)alkane(IV; X=O, Y=NO, n=2-4) have been synthesised by the nitrosation of the respective ureas in a suspension or solution of water using sodium nitrite and formic acid. The ureas were obtained by heating a mixture of amines or diamines with β-chloroethylisocyanate either in the medium of water or ethanol. The corresponding nitrosothioureas (I, II, III and IV; X=S, Y=NO) were synthesised from the respective thioureas by nitrosation using sodium nitrite and dilute hydrochloric acid (0.1 *N*) in the medium of either dichloromethane or chloroform. The dilute acid conditions were selected so as to favour the formation of unprotonated nitrous acid and N_2O_3. Since these species are harder acids than the nitrosonium ion or its derivatives which is formed at a highly acidic condition, they were expected to favour electrophilic attack at the harder nitrogen of the thioureas rather at the competing soft sulphur atom. In the event, when a suspension of the thioureas and sodium nitrite in dichloromethane or chloroform at −5° was treated dropwise with one equivalent af 0.1 *N* HCl, a yellow colour is slowly developed and on normal working resulted in the isolation of the novel *N*-nitrosothioureas. When nitrosation of the thiourea was carried out at higher concentration of acid (3-5 *N*) the corresponding ureas were obtained (I, II and III; X=O, Y=H) instead of nitroso derivatives. This type of conversion of thiourea to urea in higher acidic conditions has been reported by several investigators[5].



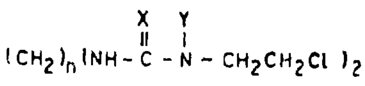
I



II



III



IV

Antitumor activity : A few nitrosourea and nitrosothiourea derivatives have been screened for their

† Part-VIII, *Indian J. Chem., Sect. B*, 1984, 23, 127.

antitumor activity by *in vivo* against the transplanted mouse leukemia L1210 by using the method reported by Bradner *et al*[6]. The compounds were administered in an olive oil suspension for 8 days consecutively using *N,N*-bis(2-chloroethyl)-*N*-nitorsourea (BCNU) as standard. The antitumor activity of the compounds was evaluated by measuring the median survival time whose results were expressed as percent T/C (MST treated/MST control) × 100. The test results have been shown in Table 2. Among the compounds tested, **III** (X = S, Y = NO, n = 4) was found to be the most active inhibitor against leukemia L1210 in producing long term survival. The percent T/C value of this compound was found to be 470 in a dose of 16 mg/kg of the body weight of the mouse.

TABLE 2—EFFECT OF NITROSO DERIVATIVES ON L1210 LEUKEMIA*

Dose mg/kg	III (X=O, Y=S, n=4) TC %	III (X=O, Y=S, n=4) Surv.	III (X=S, Y=O, n=4) TC %	III (X=S, Y=O, n=4) Surv.
1	104	0	94	1
4	240	1	100	1
8	470	3	162	0
16	470	6	200	0
32	156	0	200	0

* Tumor inoculum : 10^4 leukemia cell per mouse implanted ip , Treatment : single dose ; Evaluation : median survival time (MST) ; Result TC = MST treated/MST control × 100 ; Criteria, TC more than 120 significant block ; Surv. = Number of mice surviving at 30 days.

Experimental

The ir spectra were taken on Perkin-Elmer 293 spectrophotometer.

3-(4-Phenylthiazolyl-2)-1-(2-chloroethyl)urea (**I** ; R = C_6H_5, X = O, Y = H) : A mixture of 2-amino-4-phenylthiazole (1.8 g) and 2-chloroethylisocyanate (1.1 ml) in a suspension of water was heated on water bath for 1 h during which a clear solution was obtained. After cooling it was stirred overnight and the precipitate, thus obtained, was filtered, dried and crystallised from ethanol to yield the product (1.2 g, 36%,) m.p. 120-122° (Found : S, 11.18. $C_{12}H_{12}N_3SOCl$ requires S, 11.38%) ; ν_{max} (KBr) 3320 (br., NH), 2920 (CH_2 stretching), 1700 (C=O) and 1600 cm^{-1} (C–N stretch).

Similarly, **I** (R = *p*-chlorophenyl, X = O, Y = H), m.p. 116° ; **II** (X = O, Y = H), m.p. 164-167° ; **III** (n = 4, X = O, Y = H), m.p. 80° ; **III** (n = 5, X = O, Y = H), m.p. 122° ; **III** (n = 6, X = O, Y = H), m.p. 119° ; **IV** (n = 2, X = O, Y = H), m.p. 144° ; **IV** (n = 3, X = O, Y = H), m.p. 192° and **IV** (n = 4, X = O, Y = H), m.p. 204° have been prepared from their respective amines.

3-(4-Phenylthiazolyl-2)-1-(2-chloroethyl)thiourea (**I** ; X = S, Y = H) : A mixture of 2-amino-4-phenylthiazole (1.8 g) and 2-chloroethylisocyanate (1.5 ml) in absolute alcohol (20 ml) was refluxed for 1 h. After cooling, the desired product was separated as colourless crystals (1.8 g, 60%), m.p. 186° (Found : S, 21.25. $C_{12}H_{12}N_3S_2Cl$ requires S, 21.47%) ; ν_{max} (KBr) 3300 (br., NH), 2900 (CH_2 stretching), 1600 cm^{-1} (C–N stretch).

Similarly, **II** (X = S, Y = H), m.p. 206° (Found : S, 21.22. $C_{10}H_{10}N_3S_2Cl$ requires S, 23.53%) ; **III** (n = 4, X = S, Y = H), m.p. 145° (Found : S, 15.30. $C_8H_{15}N_3SCl$ requires S, 15.46%) ; **III** (n = 5, X = S, Y = H), m.p. 175° (Found : S, 14.18. $C_9H_{17}N_3SCl$ requires S, 14.74%) ; **III** (n = 6, X = S, Y = H), m.p. 181° (Found : S, 13.60. $C_{10}H_{19}N_3SCl$ requires S, 13.85%) ; **IV** (n = 2, X = S, Y = H), m.p. 127° (Found : S, 21.30. $C_8H_{16}N_4S_2Cl_2$ requires S, 21.12%) ; and **IV** (n = 3, X = S, Y = H), m.p. 166° (Found : S, 20.25. $C_9H_{18}N_4S_2Cl_2$ requires S, 20.18%) were prepared.

3-(4-Phenylthiazolyl-2)-1-(2-chloroethyl)-1-nitrosourea (**I** ; R = C_6H_5, X = O, Y = NO) : To a solution of the **I** (R = C_6H_5, X = O, Y = H) (1.2 g) in 85% formic acid (30 ml) sodium nitrate (1.1 g) was added under ice-cooling with stirring. After 1 h, it was diluted with equal volume of water and kept overnight. The desired compound separated as colourless crystals (0.6 g, 35%), m.p. 247° (Found : S, 10.08. $C_{12}H_{11}N_4SO_2Cl$ requires S, 10.27%) ; ν_{max} (KBr) 3350 (br., NH), 2900 (CH_2 stretch), 1700 (C=O) and 1540 cm^{-1} (C–N stretch).

3-(4-Phenylthiazolyl-2)-1-(2-chloroethyl)-1-nitrosothiourea (**I** ; R = C_6H_5, X = S, Y = NO) : To a suspension of the thiourea (**I** ; R = C_6H_5, X = S) (0.30 g) and sodium nitrite (0.2 g) in dichloromethane (100 ml), dilute HCl (20 ml, 0.1 *N*) was added dropwise with stirring at 0° for 0.5 h. After the addition was completed the reaction mixture was warmed with stirring and kept overnight at room temperature. The organic layer was removed, dried over anhydrous Na_2SO_4 and solvent evaporated. The crude nitrosothiourea was purified by crystallisation in cold ethanol (0.2 g, 60%), m.p. 207° (Found : S, 18.32. $C_{12}H_{11}N_3S_2OCl$ requires S, 18.54%).

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF NITROSO DERIVATIVES

Compd. no.	Nitroso ureas, I (X=O, Y=NO) M.p.	Nitroso ureas, I (X=O, Y=NO) %Sulphur Found/(Calcd.)	Nitroso thioureas, I (X=S, Y=NO) M.p.	Nitroso thioureas, I (X=S, Y=NO) %Sulphur Found/(Calcd.)
I, R = *p*-chlorophenyl	256	8.73 (8.91)	>250	17.19 (17.07)
II	>250	11.05 (11.22)	>250	21.12 (21.26)
III, n = 4	72*	18.72** (19.09)	231	13.36 (13.58)
III, n = 5	90*	—	225	12.54 (12.80)
III, n = 6	110*	—	246	12.26 (12.12)
IV, n = 2	144*	25.68** (25.53)	194	17.58 (17.78)
IV, n = 3	165*	—	205	17.14 (17.06)

* Recrystallised from petroleum ether.
** Nitrogen %.

The other nitrosoureas and nitrosothioureas have been listed in Table 1.

When the nitrosation was carried out by the gradual addition of HCl (3 *N*) by taking the above thiourea and sodium nitrite in eqivalent proportions, a deep red colouration developed which gradually turned bluish, and after heating to room temperature, fine particles of sulphur appeared on the surface. These were separated and usual work up procedure with the organic layer gave a colourless solid which was found to be identical to **1** ($R=C_6H_5$, $X=O$, $Y=H$).

Acknowledgement

The authors are grateful to Prof. G. Bianchi University of Pavia, Italy for his help in carrying out the antitumor activity test and to C.S.I.R., New Delhi for providing fellowship to one of them (J.S.).

References

1. J. A. MONTOMERY, *J. Med. Chem.*, 1980, **23**, 1063.
2. C. HANSCH, A. LEO, C. SCHMIDT, P. C. C. JOW and J. A. MONTGOMERY, *J. Med. Chem.*, 1980, **23**, 1095.
3. T. P. JOHNSTON, C. S. MCCALEB and J. A. MONTGOMERY, *J. Med. Chem.*, 1975, **18**, 104.
4. P. A. FOX, L. C. PANESCI and P. S. SCHEIN, *Cancer Res.*, 1977, **37**, 783.
5. L. FIELD, R. V. DELTS, R. RAVINDRAN, P. G. LENHERT and G. E. CARNAHAN, *J. Chem. Soc., Chem. Commun.*, 1978, 249.
6. W. T. BRADNER and D. J. HUTCHINSON, *Cancer Chemother. Rep.*, 1966, **50**, 79.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 985-990

Solvent Effects on Electronic Spectra of Some Amino Salts of d-Camphor-β-Sulphonic Acid

S. K. KHANNA, B. C. PANT and H. P. TIWARI*

Department of Post-Graduate Studies and Research in Chemistry, Rani Durgavati Vishwavidyalaya, Jabalpur

The electronic spectra of amino salts of d-camphor-β-sulphonic acid were examined in a series of solvents covering a wide range of polarity. The transition energies (E_T) were plotted against Z-values, a solvent polarity parameter. A linear relationship was observed between transition energy and Z-value for the $n \rightarrow \pi^*$ transition. Solvent sensitivities of the amino salts have also been calculated and found to be in the increasing order as the inductive nature of the side chain increases, with the anomaly in ammonium salt. The anomaly in ammonium salt has been explained in terms of hydrogen bonding.

CAMPHOR-β-sulphonic acid is a strong monobasic acid and its salts generally do not undergo hydrolysis. The ketonic group is common to all the amino derivative of d-camphor-β-sulphonic acid. The low intensity uv absorption of saturated keto compounds has been undeservedly ignored by many organic chemists. The only complete study of the simple keto compounds is that of Maroni[1], who measured the uv maxima of 32 alkyl ketones in three sovents, hexane, ethanol and water. Ignorance of appreciable solvent effect on many electronic transitions has often led to the failure to mention the solvent used in the uv measurement. Solvents often have a considerable effect on the uv spectra of organic compounds. These solvent effects are useful in determining the electronic transition and to find out different types of solute-solvent interactions[2]. Kosower[3] has developed a solvent polarity parameter, Z, which has been used successfully in correlating a number of solvent effects on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The present investigation was undertaken with a view to studying the effect of solvents of varying polarity on the electronic transition of amino salts of d-camphor-β-sulphonic acid. An attempt has been made to analyse the results in terms of solvent polarity parameter Z. It is observed that Z-values are useful in the analysis of the results.

Experimental

Chemicals : Compounds were prepared as described by Pant[4]. All the solvents used were of either B.D.H., AnalaR or E.M., G.R. quality. Freshly distilled[5] solvents were used in all the experiments.

Spectra : The absorption spectra were recorded using very dilute solutions of the compounds at 26±1°, on a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer. The molecular extinction coefficients, ϵ, were calculated from the observed values of absorption at different wavelengths.

The oscillator strength, 'f' was calculated from the following relation : $f = 4.32 \times 10^{-9} \int \epsilon d\nu$, utilising $\epsilon_{max}^{\Delta \bar{\nu}} = \int \epsilon \, d\nu$,

where $\Delta \bar{\nu}$ is the half bandwidth in wave numbers. The transition energy, E_T was calculated from the relation

$$E_T(\text{kcal mol}^{-1}) = \frac{2.859 \times 10^5}{\lambda_{max} \times (\text{Å})}$$

The spectra methylamine, ethylamine, ethanolamine, dimethylamine, isopropylamine and n-propylamine salts of d-camphor-β-sulphonic acid were measured in a series of solvents, varying in polarity from chloroform (Z, 63.2) to water (Z, 94.6). The results are summarized in Tables 1-4. The transition energies in different solvents are plotted against Z-values (Figs. 1-7).

Results and Discussion

It is well known that simple aliphatic aldehydes and ketones usually exhibit a weak absorption band with fine structure in the range 230-350 nm and have maximum absorption in the region 280-300 nm ($\epsilon_{max} \simeq 10, f \simeq 10^{-4}$). This band is attributed to the one electron singlet-singlet transition from non-bonding p-orbital to the antibonding π-orbital, namely the (s-s) $n \rightarrow \pi^*$ transition. This transition in carbonyl compounds is forbidden[6]. It is evident from the results (Tables 1-4), that all the amino-derivatives of d-camphor-β-sulphonic acid exhibit weak absorption maximum in the range 285-290 nm. The band has been assigned to $n \rightarrow \pi^*$ carbonyl transition, on the basis of the following criteria : (i) low band intensity, (ii) blue shift of the band with increasing solvent polarity and (iii) obliteration of vibrational fine structure on changing from non-polar to polar media[7].

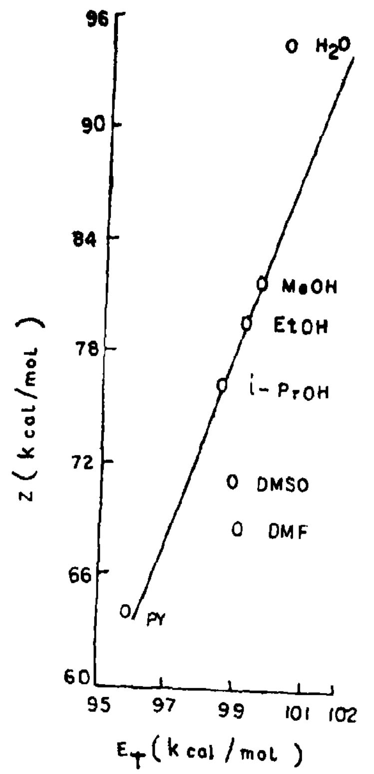


Fig. 1. Ammonium salt of d-camphor-β-sulphonate.

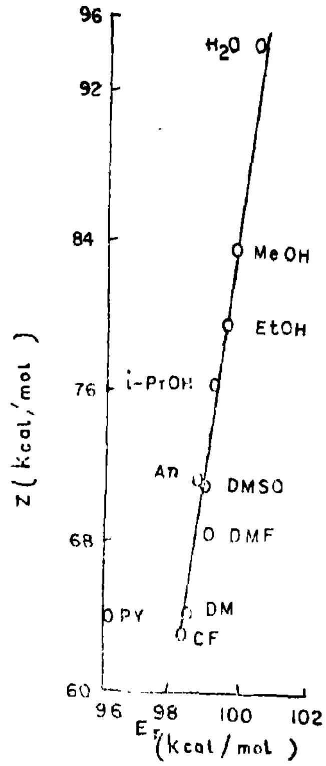


Fig. 3. Ethylamino-d-camphor-β-sulphonate.

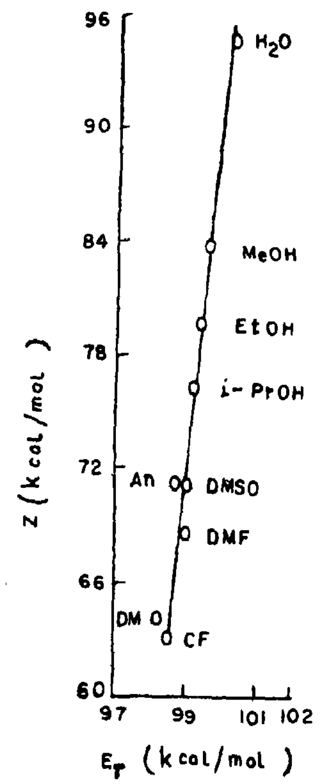


Fig. 2. Methylamino-d-camphor-β-sulphonate.

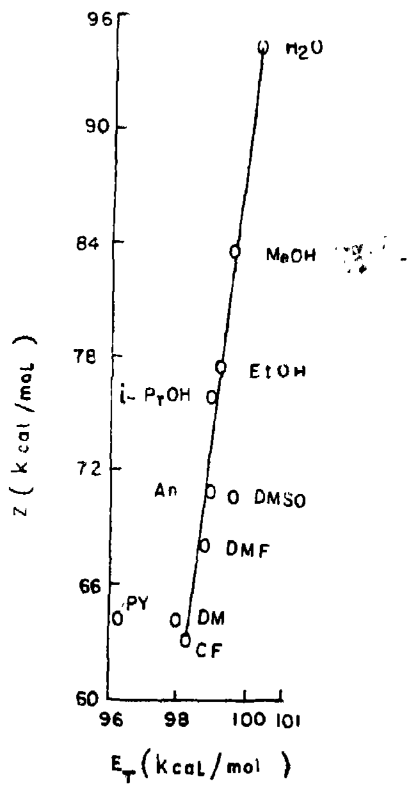


Fig. 4. Dimethylamino-d-camphor-β-sulphonate.

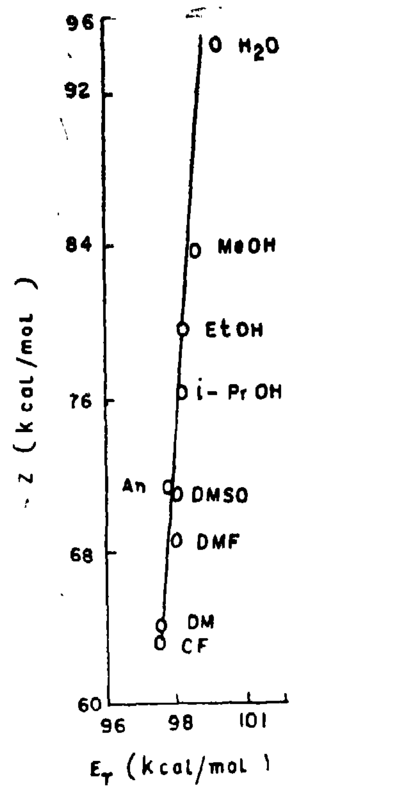


Fig. 5. n-Propylamino-d-camphor-β-sulphonate.

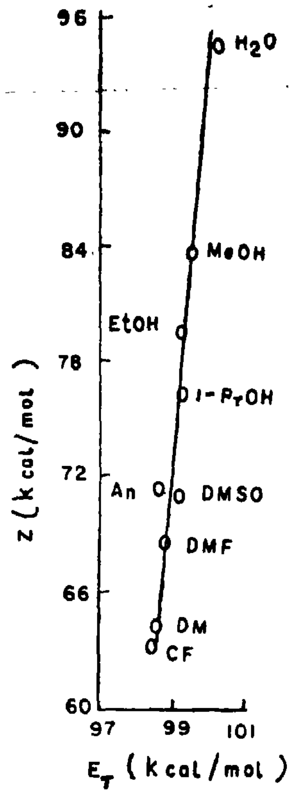


Fig. 7. Ethanolamino-d-camphor-β-sulphonate.

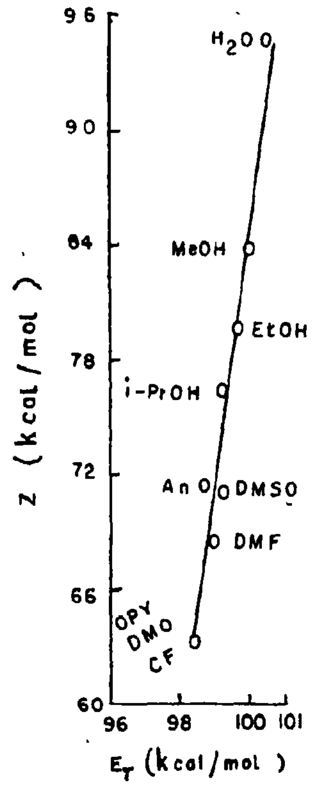


Fig. 6. Isopropylamino-d-camphor-β-sulphonate.

TABLE 1—SPECTRAL DATA ON AMMONIUM SALT OF d-CAMPHOR-β-SULPHONIC ACID

Sl. no.	Solvent	Z	Dielectric constant	λ_{max}	ϵ_{max}	E_T k cal mol^{-1}	f
1.	Dioxane*	—	2.21	—	—	—	—
2.	Chloroform* (CF)	68.2	5.06	—	—	—	—
3.	Dichloro*-methane (DM)	64.2	9.04	—	—	—	—
4.	Pyridine (Py)	64.0	12.30	290	34.98	98.58	—
5.	Isopropanol (i-PrOH)	76.3	18.30	290	25.00	98.58	1.080
6.	Ethanol (EtOH)	79.6	24.30	288	35.00	99.27	2.420
7.	Methanol (MeOH)	83.6	32.60	287	31.25	99.62	1.360
8.	Acetonitrile* (An)	71.3	36.20	—	—	—	—
9.	Dimethyl formamide (DMF)	68.5	37.00	289	31.00	98.93	1.311
10.	Dimethyl sulphoxide (DMSO)	71.1	46.60	289	81.25	98.98	1.481
11.	Water (H_2O)	94.6	80.00	285	40.62	100.32	3.760

* Ammonium salt of d-camphor-β-sulphonic acid not soluble.

Examination of these results shows that on changing the solvent from chloroform to water, the $n \rightarrow \pi^*$ transition band exhibits a small blue shift. The $n \rightarrow \pi^*$ transitions observed in different solvents are very

TABLE 2—SPECTRAL DATA ON d-CAMPHOR-β-SULPHONIC ACID SALTS

Solvent*	Methylamine salt λ_{max} nm	ϵ_{max}	E_T kcal mol^{-1}	f $\times 10^5$	Dimethylamine salt λ_{max} nm	ϵ_{max}	E_T kcal mol^{-1}	f $\times 10^4$
Dioxane	290.0	19.375	98.58	0.569	290.0	21.50	98.58	0.750
CF	290.1	37.000	98.58	2.877	291.0	35.00	98.25	2.327
DM	291.0	33.750	98.24	2.223	292.0	53.13	97.91	5.586
Py	—	—	—	—	297.0	1268.8	96.26	—
i-PrOH	288.0	23.125	99.27	0.850	289.0	26.88	98.93	1.168
EtOH	287.5	28.125	99.47	1.242	287.5	38.75	99.27	3.645
					226.0	30.00		
MeOH	287.0	33.75	99.62	2.412	287.0	36.25	99.62	2.526
An	289.5	25.00	98.75	0.918	289.0	26.25	98.93	1.043
DMF	288.5	19.00	99.10	0.399	289 0	32.62	98.93	1.254
DMSO	289.0	19.00	98.93	0.426	287.5	16.25	99.62	0.245
H_2O	285.0	33.77	100.32	0.157	285.0	45.00	100.32	4.663

* Abbreviation as in Table 1.

TABLE 3—SPECTRAL DATA ON d-CAMPHOR-β-SULPHONIC ACID SALTS

Solvent*	Ethylamine salt λ_{max} nm	ϵ_{max}	E_T kcal mol^{-1}	f $\times 10^4$	n-Propylamine salt λ_{max} nm	ϵ_{max}	E_T kcal mol^{-1}	f $\times 10^5$
Dioxane	290.0	21.125	98.52	0.643	290.0	26.250	98.58	1 010
CF	290.0	30.000	98.58	1.872	290.0	37.500	98.58	3.013
DM	290.0	37.500	98.58	1.247	290.0	37.500	98.58	2.397
Py	297.0	1268.75	96.28	—	—	—	—	—
i-PrOH	288.0	21.250	99.27	0.698	288.0	25.500	99.27	1.432
EtOH	287.0	31.250	99.62	1.998	288.0	36.250	99.27	2.959
MeOH	286.0	42.500	99.96	4.378	28.70	38.500	99.62	3.659
An	289.5	25.000	98.76	0.907	289.5	26.687	98.76	1.145
DMF	289.0	31.000	98.93	1.473	288.5	25.000	99.10	0.583
DMSO	288.0	18.000	99.27	0.406	288.5	29.317	99.10	1.211
H_2O	285.0	47.500	100.32	5.270	285.0	37.500	100.32	3.175

* Abbreviation as in Table 1.

TABLE 4—SPECTRAL DATA ON d-CAMPHOR-β-SULPHONIC ACID SALTS

Solvent*	Isopropylamine salt λ_{max} nm	ϵ_{max}	E_T kcal mol^{-1}	f $\times 10^5$	Ethanolamine salt λ_{max} nm	ϵ_{max}	E_T kcal mol^{-1}	f $\times 10^4$
Dioxane	290.0	20.000	98.58	0.674	290.0	21.250	98.58	0.778
CF	291.0	38.750	98.25	2.880	290.5	43.750	98.42	4.287
DM	292.0	58.370	97.91	7.812	290.0	35.000	98.58	3.786
Py	297.0	1268.12	96.26	—	—	—	—	—
i-PrOH	288.0	28.875	99.27	1.485	288.0	23.770	99.27	0.854
EtOH	287.0	41.375	99.62	3.918	288.0	43.770	99.27	4.285
MeOH	286.0	45.000	99.96	5.050	287.0	47.000	99.62	5.613
An	289.5	25.000	98.76	0.918	289.5	29.120	98.76	1.446
DMF	288.5	81.000	99.10	1.078	289.0	29.120	98.93	0.969
DMSO	288.5	26.250	99.10	1.089	288.0	18.750	99.27	0.854
H_2O	285.0	46.250	100.32	5.140	285.0	43.750	100.32	4.205

* Abbreviation as in Table 1.

similar in character and occur in approximately the same wavelength range. The spectra obtained in various solvents reveal a single smooth band in the region of their longest wavelength maximum and the band changes in a fairly smooth manner with solvents, that is, there are no changes in the shape of curves. Dimethylamine salt shows an additional low intensity peak at 226 nm in ethanol, which seems to be due to general absorption of the saturated molecule. The intensities of the $n\rightarrow\pi^*$ bands are also considerably influenced by the solvent and specially the integrated intensity in water is much large than in any other solvent (Tables 1-4).

The transition energies of these amino-derivatives of d-camphor-β-sulphonic acid in various solvents are plotted against Z-values (Figs. 1-7). A moderately good linear relationship has been observed between

the band position (as transition energies) and the Z-values for solvents. In the case of methylamine, ethylamine, and n-propylamine salts, linearity is strikingly good (with an average deviation of ± 0.15 kcal mol^{-1} of the points from the straight line). This linear relationship may be taken as a support for the electrical parallelism between the $n \rightarrow \pi^*$ transition and the charge transfer transition which defines the Z-value. Furthermore, it may be concluded that the derivatives are rigid cyclic carbonyl compounds[8,9].

The amino salts of d-camphor-β-sulphonic acid in the nonhydroxyl solvent pyridine, show marked differences between the calculated and actual values of transition energies, and thus are indicative of specific solute-solvent interactions. The transition in pyridine requires less energy than predicted from plots of E_T *vs* Z (2.42, 2.0308 and 2.0 kcal mol^{-1}, in ethylamine, isopropylamine and dimethylamine salts, respectively). The nitrogen atom in pyridine may act as donor and may form charge transfer complexes with these derivatives, resulting in the lowering of the transition energy.

A low value of transition energy in acetonitrile compared to DMF and DMSO may be attributed to less effective hydrogen bonding than either in DMF or DMSO. The stronger the hydrogen bond in $n \rightarrow \pi^*$ transition, the higher is the transition energy[10]. In the case of hydroxylic solvents, bluo shifts are found to decrease in the order, $H_2O > CH_3OH > C_2H_5OH > i\text{-}C_3H_7OH$. This effect of hydroxylic solvents is attributed, at least partly, to the hydrogen-bonding between solute and solvent mloecules. The carbonyl oxygen in Rechler's acid derivatives with lone pair of electrons acts as electron donor to the hydrogen of the hydroxyl group of the solvent molecule. Thus, it is evident that the extent of solute-solvent hydrogen bonding is apparently dependent on the acidity of alcohol. A similar trend has been found by Chandra and Basu[11].

Brealy and Kasha[10] pointed out that hydrogen bonding lowers the energy of n-orbital by an amount approximately equal to the energy of hydrogen bond. But Pimentel[12] has shown, in his analysis of solvent effects, that the magnitude of blue shift of the $n \rightarrow \pi^*$ transition is not a direct measure of the energy of hydrogen-bonding between solute and solvent. Kosower[8] developed a simple model of the transitions which permits an estimate of the hydrogen bonding energy from uv spectral data. If we consider the excited state of $n \rightarrow \pi^*$ transition as represented by the structure I, and make the simplifying assumption that the polarization already present in the ground state II, is unaffected by the excitation, the resultant dipole moment for the excited state will be very close to zero. This will then be analogous to that of the 1-alkylpyridinium iodide complexes in which the destabilization of the excited state upon transfer of the complex dipole from one solvent to another was equal to the stabilization of the ground state[8]. The hydrogen bonding energy is estimated as half of the change in transition energy from the gas phase or more simply from a non-polar solvent (dioxane in our case) to the polar solvent.



I II

The hydrogen bonding or, more simply, interaction energies based on the above model have been calculated for the following compounds in water: methylamine salt (0.866), ethylamine salt (0.866), dimethylamine salt (0.866), isopropylamine salt (1.034) and ethanolamine salt (0.949), with the values of energy (kcal mol^{-1}) in parentheses.

The solvent sensitivity of the $n \rightarrow \pi^*$ transition, which is a measure of the degree to which the position of the $n \rightarrow \pi^*$ transition responds to the polarity of the solvent, can be obtained as an experimental measure, as the difference between transition energies, E_T(water) − E_T(chloroform)[13]. The solvent sensitivity can also be evaluated from the product of a slope 'm' (of the least square line drawn to relate points in Figures, with respect to Z, *i.e.* $m = dE_T/dZ$), and Δ Z, which is the difference in the Z-values of water and chloroform. The solvent sensitivities of the isopropylamine salt and dimethylamine salt are slightly higher than the other salts (Table 5). The other salts show small variations in the overall solvent sensitivity which decreases in the order, ammonium > ethanolamine > n-propylamine > ethylamine > methylamine salts.

TABLE 5 – SOLVENT SENSITIVITIES OF AMINO SALTS OF d-CAMPHOR-β-SULPHONIC ACID

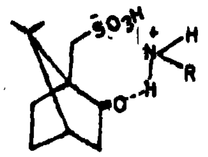
Compound	$n \rightarrow \pi^*$ Transition		
	E_T† kcal mol^{-1}	m	$m\Delta Z$* kcal mol^{-1}
Ammonium salt	1.740	0.121	2.214
Methylamine salt	1.740	0.064	2.010
Ethylamine salt	1.740	0.066	2.072
n-Propylamine salt	1.740	0.067	2.104
Isopropylamine salt	2.070	0.083	2.597
Dimethylamine salt	2.070	0.076	2.370
Ethanolamine salt	1.900	0.066	2.070

† Defined as difference between water and chloroform transition energies.

* Numbers of this column should be compared with those under ΔE_T.

The above order of solvent sensitivities reveals that as the inductive nature (+I) of the side chain increases the solvent sensitivity increases. The ammonium salt is anamalous. A possible explanation for the decrease in solvent sensitivities may be given on the basis of intra-molecular hydrogen bonding between the ketonic group and hydrogen atoms attached to nitrogen (structure III). The replacement of a methyl group by an ethyl group must weaken intra-molecular hydrogen bonding and thus permit a somewhat more highly organized cybotactic region in ethylamine salt. In isopropylamine and dimethylamine salts the greater solvent sensitivity can also be attributed to the same reason,

as in these cases the electron density on the nitrogen atom will be more than in other salts, thus making



III

R=H, $-CH_3$, $-C_2H_5$, n-C_3H_7, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH-$, $-C_2H_4OH$, n-C_5H_{11}, $-CH_2-CH=CH_2$.

the intra-molecular hydrogen bonding even more difficult. Yoshida *et al.*[14] have also shown in the case of anthraquinones, that 1-aminoanthraquinone forms stronger inter- as well as intra-molecular hydrogen bonding than 1-methylamine and 1-dimethylamine anthraquinone. These Rechler's acid derivatives are capable of forming intra- as well as inter-molecular hydrogen bondings. The inter-molecular hydrogen bonding will be most favoured in the ammonium salt, resulting in the higher solvent sensitivity.

References

1. P. Maroni, *Ann. Chim.*, 1957, **13**, 2 ; P. Maroni and J. E. Dubois *J. Chem. Phys.*, 1954, **51**, 402.
2. H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy", John Wiley, New York, 1962, pp. 186, 206.
3. E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3261.
4. B. C. Pant, Ph.D. Thesis, Agra University, 1960.
5. "Technique of Organic Chemistry", eds. E. S. Weissberger, J. A. Proskaur, Riddick and E. E. Toops, Jr., Vol. 7, Interscience, New York, 1954.
6. H. Suzuki, "Electronic Spectra and Geometry of Organic Molecules", Academic Press, N. R., 1967, p. 75.
7. J. W. Sidman, *Chem. Rev.*, 1958, **58**, 689.
8. E. M. Kosower, G. S. Wu and J. S. Sorensen, *J. Am. Chem. Soc.*, 1961, **83**, 3147.
9. E. M. Kosower and D. C. Remy, *Tetrahedron*, 1959, **5**, 281.
10. G. L. Brealy and M. Kasha, *J. Am. Chem. Soc.*, 1955, **77**, 4462.
11. A. K. Chandra and S. Basu, *Trans. Faraday Soc.*, 1960, **56**, 632.
12. G. C. Pimentel, *J. Am. Chem. Soc.*, 1958, **80**, 3263.
13. E. M. Kosower and G. S. Wu, *J. Am. Chem. Soc.*, 1961, **83**, 3142.
14. Z. Yoshida and F. Takabayshi, *Tetrahedron*, 1968, **23**, 983.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 991-995

Evaluation of New Substituent Parameters to Explain ^{13}C Chemical Shift for *para*-Substituents in Benzene Ring

L. R. NAYAK**, B. K. MISHRA and G. B. BEHERA*

Department of Chemistry, Sambalpur University, Jyoti Vihar, Burla-768 017

The ^{13}C chemical shift data of 1,4-disubstituted benzenes have been used to evaluate *para*-substituent constants (α_X^4 and β_X^4) and their applicability has been examined in 39 different sets of data. These parameters have been found highly suitable to correlate the ^{13}C chemical shifts of aromatic, aliphatic and heterocyclic systems.

EXTENSIVE correlation of ^{13}C chemical shifts in mono-substituted benzenes with Hammett's σ^1 constants has been reported by Spiesecke and Schneider[2] for the first time following the work of Lauterber[3,4]. Other parameters[5] used for the correlation are σ_P^o, σ_P^+ and σ_R^o. Good correlations have been observed[6] with σ_P^+ for substituent at *para*-position. However, analysis of extensive experimental data shows that Hammett equation fails for charged substituents[7]. Correlations of substituent chemical shift for *ortho*- and *meta*-substituents in benzene with σ have been found to be unsatisfactory[6]. Use of single parameter for correlation with substituent chemical shift has been criticised. The reason for the failure of the use of one substituent parameter is that the constituent factors (polar and mesomeric) sometimes differ widely in magnitude in different systems.

Taft[5] applied dual substituent parameters with inductive (field) effect (σ_I) and resonance effect (σ_R). Topsom[8] has summarised the advantages of the use of dual substituent parameters (DSP) analysis in the interpretation of spectroscopic data. DSP analysis of benzene substituent chemical shift for *para*-position has been made with varieties of substituent parameters. Parameters used are σ_I and σ_R^o by Taft *et al.*[5,9,10], F and R (Swain-Lupton's parameter) by Bodner and Todd[12], σ_I and σ_R by Coulson[13]. Godfrey[14] has introduced three new parameters, F (a coulombic field effect, having no relation with traditional field parameters), T (a charge transfer effect) and S (overlap field). Correlation of benzene chemical shift values with F and R (Swain-Lupton's parameter) and Q[15] (a semiemperical parameter) have been found to be successful[16]. Dewar *et al.*[17] have proposed a triple parameter model involving contribution from field (F), mesomeric (M) and mesomeric-field (MF) effects to correlate the substituent effect and is known as FMMF method. However, the correlation of benzene chemical shift by FMMF method has been found to be unsatisfactory[18]. Reynolds and Hammer[19] have shown the limitations of FMMF method. In this work an attempt has been made to derive some new substituent parameters for substituents at position-4 in the benzene ring using the nmr chemical shift values.

Evaluation of parameters :

To facilitate the statistical analysis in this work the ^{13}C chemical shift values of C-4 in 1,4-disubstituted benzene[20] (1) have been given in Table 1. This data set is called 'training set'. An examination

$$\overset{1}{X}-C_6H_4-\overset{4}{Y}$$

1

of the training set reveals that (i) the C-4 chemical shifts of a column-set vary in the same order for all substituents at position-4, (varying Y) for all values of X, (ii) the chemical shift values of a row-set also depends on the nature of the substituent, X. To explain the chemical shift values (δ) equation (1) is proposed, which describes the influence of the variance of a substituent, X with respect to H for the same substituent Y at C-4.

$$\delta_{XY} = \alpha_X^4 \delta_{HY} + \beta_X^4 \qquad (1)$$

In this equation δ_{XY} is the ^{13}C chemical shift values of compounds with varying Y substituent and fixed X, δ_{HY} is the chemical shift values of such compounds, where X=H. The α_X^4 is the sensitivity index for the *para*-substituent X on the C-13 chemical shift at C-4 and the β_X^4 value is constant for a particular column and varies with the nature of the substituent, X. Values of α_X^4 and β_X^4 are calculated from the data set given in Table 1 by least square method in a DCM-1101 microcomputer. The values of α_X^4 and β_X^4 are given in Table 2 along with the other statistical parameters.

General feature of parameters :

The α_X^4 and β_X^4 values thus evaluated are found to have almost an inverse relationship to each other. Values of α_X^4 are less than one for electron donating substituents, like NMe_2, NH_2, OMe, F, Cl, Br and Me, and more than one for electron withdrawing substituent, like CF_3, CN, COOEt, COMe, NO_2 and CHO, the hydrogen having the value one.

** Department of Physics, Panchayat College, Bargarh-768 028.

TABLE 1—TRAINING SET

Sl. no.		NMe_2	NH_2	OMe	F	Cl	Br	Me	H	CF_3	CN	COOEt	COMe	NO_2	CHO
1.	NMe_2	144.08	144.81	145.71	147.44	148.98	149.47	148.80	150.59	152.14	152.38	153.16	153.31	154.01	154.23
2.	NH_2	137.87	188.55	139.87	142.36	144.86	145.39	143.70	146.22	149.35	150.44	150.69	151.08	152.43	152.49
3.	OMe	152.04	152.69	153.34	155.68	158.16	158.63	157.24	159.52	162.00	162.76	163.16	163.36	164.57	164.57
4.	F	155.62	156.28	157.19	158.75	161.22	161.77	161.00	162.82	164.61	164.96	165.61	165.64	166.20	166.48
5.	Cl	121.81	123.12	125.50	129.09	132.58	133.17	131.08	134.24	138.12	139.48	139.13	139.38	141.31	140.98
6.	Br	108.51	110.17	112.77	116.48	120.27	121.03	119.04	122.44	126.40	127.95	127.78	128 27	129.96	129.72
7.	Me	126.67	127.73	129.87	133.27	136.18	136.71	134.68	137.83	142.01	143.61	143.36	143.75	145.89	145.45
8.	H	116.62	118.51	120.63	123.92	126.41	126.81	125.26	128.31	131.98	132.66	132.73	132.98	134.49	134.88
9.	CF_3	117.80	120.01	122.85	126.45	129.08	129.72	127.83	130.62	133.97	134.53	134.24	134.33	135.91	135.62
10.	CN	97.24	99.81	103.87	108.54	110.76	111.22	109.21	112.35	116.04	116.66	116.23	116.28	118.29	117.64
11.	COOEt	117.30	120.01	122.83	126.71	128.85	129.29	127.73	130.45	133.65	134.24	134.09	134.19	135.84	135.11
12.	COMe	125.21	127.68	130.20	133.46	135.30	135.74	134.57	137.00	139.62	139.77	140.06	140.11	141.37	141.13
13.	NO_2	137.16	139.13	141.50	144.42	146.44	147.05	146.12	148.26	149.96	150.01	150.49	150.35	151.03	151.13
14.	CHO	125.01	127.88	129.96	132.96	137.93	135.06	134.14	136.87	138.65	138.70	139.19	138.94	140.04	140.01

TABLE 2 – VALUES OF SUBSTITUENT PARAMETERS α_x^+ AND β_x^+ AS PER EQUATION (1)

Sl. no.	Substituent	α_x^+	β_x^+	γ	SD
1.	NMe_2	0.85	30.37	0.998	0.9151
2.	NH_2	0.84	30.61	0.997	1.1533
3.	OMe	0.92	17.08	0.999	0.7320
4.	F	0.98	6.94	0.999	0.6679
5.	Cl	0.99	2.53	0.998	0.9144
6.	Br	0.99	2.00	1.000	0.1779
7.	Me	0.97	6.66	1.000	0.3186
8.	H	1.00	0.0	1.000	—
9.	CF_3	1.04	−9.11	0.999	0.7049
10.	CN	1.05	− 10.75	0.997	1.2069
11.	COOEt	1.03	−8.09	0.998	0.9911
12.	COMe	1.03	−8.27	0.997	1.1879
13.	NO_2	1.05	−12.63	0.992	1.8019
14.	CHO	1.04	−10.97	0.995	1.5107

The β_x^+ values do not exhibit any regularity except that electron donor substituents show positive values and electron acceptor substituents show negative values, Zero being the value for hydrogen as the substituent. The β_x^+ values have a greater variance than the α_x^+ values. To examine, if these α_x^+ and β_x^+ values have any collinearity with other known parameters (P), equation (2) has been written.

$$\alpha_x^+ \text{ or } \beta_x^+ = AP + B \qquad (2)$$

Parameters (P) correlated are Swain-Lupton's F, R ; σ_p^+, Taft's σ_I, σ_R and Es[21]. In equation (2), B is the intercept and A is the coefficient of the parameter P. Again α_x^+ and β_x^+ are individually correlated with F and R and σ_I and σ_R by a DSP equation (3),

$$\alpha_x^+ \text{ or } \beta_x^+ = A_1P_1 + A_2P_2 + B' \qquad (3)$$

where A_1 and A_2 are coefficients of parameters P_1 and P_2, respectively, and B' is the intercept. The statistical parameters derived from equations (2) and (3) are given in Tables 3 and 4, respectively.

A close analysis of Table 3 and 4 reveals that both α_x^+ and β_x^+ have a better relation with resonance than field effect. A DSP analysis, though improves the correlation, does not bring the level of correlation to 0.99. Further addition of useful parameters involving magnetic effect, charge density effect may improve the correlations. Since the quantification of these effects sometime becomes a vexing problem, it is proposed that α_x^+ and β_x^+ can be taken as useful parameters to predict the chemical shift values.

TABLE 3—RELATION OF α_x^+ AND β_x^+ WITH DIFFERENT PARAMETERS USING EQUATION (2)

Sl. no.		Parameter	A	γ	SD	B	f	n
1.	α_x^+	F	0.1418	0.7006	0.521	0.9139	0.0528	14
2.	Do	R	0.1815	0.9010	0.0387	1.009	0.032	14
3.	Do	σ_p^+	0.0823	0.855	0.0385	0.9781	0.0391	13
4.	Do	σ_I	0.1643	0.5448	0.0613	0.9319	0.0621	14
5.	Do	σ_R	0.2330	0.9014	0.03161	1.0078	0.0320	14
6.	Do	E_s	−0.03584	0.4581	0.0613	0.9469	0.06278	10
7.	β_x^+	F	−29.1868	0.6929	10.9587	17.1849	0.7658	14
8.	Do	R	−37.8114	0.9018	6.5678	−2.4891	0.4589	14
9.	Do	σ_I	−62.9624	0.5249	12.9367	18.2635	0.9040	14
10.	Do	σ_R	−50.5578	0.9395	5.2028	−2.8134	0.3635	14
11.	Do	E_s	7.972	0.5005	12.1612	11.6899	0.9355	10

TABLE 4—RELATION OF α_x^4 AND β_x^4 WITH F, R AND σ_I, σ_R AS PER EQUATION (8)

Sl. no.			A_1	B_1	r	SD	C	n
1.	α_x^4	F, R	0.0738	0.1474	0.9571	0.0220	0.9161	14
2.	α_x^4	σ_I, σ_R	0.0920	0.2095	0.9469	0.0245	0.9758	14
3.	β_x^4	F, R	−14.7217	−31.006	0.9534	4.7864	5.8251	14
4.	β_x^4	σ_I, σ_R	−17.0534	−46.2501	0.9747	3.5434	3.6229	14

TABLE 5—TRAINING SETS AND TEST SETS

Training set

1. $\delta^{13}C-1$ of *para*-substituted NN dimethylaniline[a]
2. $\delta^{13}C-1$ of *para*-substituted aniline[a]
3. $\delta^{13}C-1$ of *para*-substituted anisole[a]
4. $\delta^{13}C-1$ of *para*-substituted fluorobenzene[a]
5. $\delta^{13}C-1$ of *para*-substituted chlorobenzene[a]
6. $\delta^{13}C-1$ of *para*-substituted bromobenzene[a]
7. $\delta^{13}C-1$ of *para*-substituted toluene[a]
8. $\delta^{13}C-1$ of *para*-substituted benzene[a]
9. $\delta^{13}C-1$ of *para*-substituted trifluoromethylbenzene[a]
10. $\delta^{13}C-1$ of *para*-substituted cyanobenzene[a]
11. $\delta^{13}C-1$ of *para*-substituted ethylbenzoate[a]
12. $\delta^{13}C-1$ of *para*-substituted acetophenone[a]
13. $\delta^{13}C-1$ of *para*-substituted nitrobenzene[a]
14. $\delta^{13}C-1$ of *para*-substituted benzaldehyde[a]

Test sets

15. $\delta^{13}C-9$ for 6-substituted 2-aminobenzothiazoles[b]
16. $\delta^{13}C-9$ for 6-substituted 2-methylbenzothiazoles[b]
17. $\delta^{13}C-4$ for 2-substituted benzothiazoles[b]
18. $\delta^{13}C-6$ for 2-substituted benzothiazoles[b]
19. $\delta^{13}C-8$ for 2-substituted benzothiazoles[b]
20. $\delta^{13}C-1$ for 4-substituted phenylacetylenes[c]
21. $\delta^{13}C-3$ for 1-x-isoquinolines[d]
22. $\delta^{13}C-1$ for 4-x-isoquinolines[d]
23. $\delta^{13}C-1$ for 4-substituted benzotrifluorides[e]
24. $\delta^{13}C-1$ for *para*-substituted acetophenones[f]
25. $\delta^{13}C-1$ for *para*-substituted benzylbenzenes[g]
26. $\delta^{13}C-5$ for *ortho*-substituted phenols in cyclohexane[h]
27. $\delta^{13}C-5$ for *ortho*-substituted phenols in DMSO[h]
28. $\delta^{13}C-5$ for 2-substituted pyridines[i]
29. $\delta^{13}C-6$ for 3-substituted pyridines[i]
30. $\delta^{13}C-5$ for 2-substituted pyrimidines[j]
31. $\delta^{13}C-1$ for 4-substituted phenylvinylethers[k]
32. $\delta^{13}C-1$ for 4-substituted phenylvinylsulfides[k]
33. $\delta^{13}C-1$ for 4-substituted phenylvinylselenides[k]
34. $\delta^{13}C-4$ for *para*-substituted benzamide[l]
35. $\delta^{13}C-1$ for 4-substituted styrenes[m]
36. $\delta^{13}C$ for 4-substituted α-methylstyrenes[n]
37. $\delta^{13}C$ for 4-substituted α-t-butylstyrenes[n]
38. $\delta^{13}C-9$ for 6-substituted benzothiazoles[e]
39. $\delta^{13}C-8$ for 5-substituted 2-methylbenzothiazoles[e]

a. Ref. 20. *b.* Ref. 21. *c.* Ref. 18.

d. A. VAN VELDHVIZEN, M. VAN DIJK and G. M. SANDERS, *Org. Magn. Reson.*, 1980, **13**, 105. *e.* R. A. NEWMARK and J. H. HILL, *Org. Magn. Reson.*, 1977, **9**, 589 . *f.* T. DRAKENBERG, J. M. SOMMER and R. JOST, *Org. Magn. Reson.*, 1976, **8**, 579. *g.* Y. NAKAI, T. TAKABAYASHI and F. YAMADA, *Org. Magn. Reson.*, 1980, 13, 94. *h.* W. B. SMITH and T. W. PROULUX, *Org. Magn.-Reson.*, 1976, **8**, 205. *i.* V. GALASSO, *Org. Magn. Reson.*, 1979, **12**, 318. *j.* C. J. TUNNER and G. W. H. CHEESEMAN, *Org. Magn. Reson.*, 1976, **8**, 357. *k.* W. F. REYNOLDS and R. A. MCCLELLAN, *Can. J. Chem.*, 1977, **55**, 536. *l.* B M. LYNCH, *Can. J. Chem.*, 1977, **55**, 541. *m.* G. K. HAMER, *Can. J. Chem.*, 1973, **51**, 897. *n.* G. K. HAMER, *Can. J. Chem.*, 1973, **51**, 915.

Applicabilities of parameters :

The generality of these substituent parameters (α_X^+ and β_X^+) has been examined with various data sets (set 1 to 39) using equation (4).

$$\delta_X = a\alpha_X^+ + b\beta_X^+ + \delta_X^0 \quad (4)$$

In this equation δ_X is the chemical shift values of different *para*-substituted compounds at C-4, δ_X^0 is a constant for a given set, a and b are susceptibility of α_X^+ and β_X^+ to δ_X, respectively. To see the applicability of these parameters the thirty nine sets including the training sets are given in Table 5. Statistical parameters derived from the analysis of these data when correlated with α_X^+ and β_X^+ as per equation (4) are given in Table 6. Excellent correlations are obtained in all the data sets except for sets 16, 18 and 19. These parameters (α_X^+ and β_X^+) have been used to calculate the chemical shift values of some compounds for which experimental data are not available.

For the sake of comparison, all the 39 data sets have been correlated with F, R and σ_I, σ_R for which equations (4) and (5) are written separately with the terms having the usual meaning.

$$\delta_X = pF + qR + Q \quad (5)$$

$$\delta_X = c\sigma_I + d\sigma_R + I \quad (6)$$

The statistical parameters due to these correlations have been given in Table 6. It is observed that Swain-Lupton's parameters do not work well in these sets. The parameters developed in this work, are slightly better than Taft's parameters. The f values (goodness of fit parameters) have been calculated by using the equation SD/RMS, and are given in Table 6. Taft *et al.*[30] have shown that f=0.06 or less is required for an acceptable fit for a data set with a critical selection of substituents.

Hence, α_X^+ and β_X^+ developed by an independent method of analysis are also good substituent parameters to correlate ^{13}C nmr chemical shift values of varieties of compounds.

TABLE 6—STATISTICAL ANALYSIS

A, with α_x^+ and β_x^+ parameters ; B, with F and R parameters ; C, with σ_I and σ_R parameters

Set		n	a/p/c	b/q/d	SD	δ_x^0/Q/I	r	f
1	A	14	−108.177	−0.745	0.2474	258.448	0.9978	0.00165
	B	14	2.636	7.361	1.667	149.499	0.896	0.0111
	C	14	2.149	12.028	0.877	150.404	0.9949	0.00514
2	A	14	−169.226	−1.146	0.266	815.789	0.9988	0.00182
	B	14	4.621	10.215	8.500	145.040	0.898	0.017
	C	14	4.708	16.591	0.761	152.187	0.9906	0.0096
3	A	14	−145.974	−0.987	0.172	805.584	0.9998	0.00108
	B	14	3.884	8.955	2.142	158.410	0.891	0.018
	C	14	8.409	15.029	0.446	159.514	0.995	0.00286
4	A	14	−116.768	−0.811	0.806	179.111	0.9973	0.00188
	B	14	2.640	8.450	1.774	161.835	0.904	0.0169
	C	14	2.141	13.894	0.410	162.68	0.995	0.0025
5	A	14	184.491	0.216	2.860	2.068	0.9981	0.0184
	B	14	6.089	18.970	2.798	132.809	0.922	0.029
	C	14	6.019	12.410	0.624	133.721	0.996	0.0046
6	A	14	−187.816	−1.390	0.221	810.171	0.9996	0.00103
	B	14	6.405	15.583	3.215	120.398	0.915	0.0264
	C	14	5.970	35.100	0.711	122.03	0.996	0.0058
7	A	14	138.396	0.230	2.835	0.368	0.9975	0.0214
	B	14	6.429	13.238	2.993	136.193	0.908	0.0217
	C	14	6.198	22.108	0.461	137.78	0.997	0.00335
8	A	14	−144.424	−1.692	0.194	272.672	0.9995	0.00152
	B	14	5.340	12.658	2.540	126.566	0.920	0.0198
	C	14	5.271	20.248	0.551	127.809	0.996	0.00432
9	A	14	−81.572	−0.791	0.408	211.915	0.998	0.0030
	B	14	5.276	12.854	2.152	128.566	0.942	0.0166
	C	14	5.683	19.556	1.031	129.568	0.987	0.00796
10	A	14	−106.477	−0.971	0.808	216.218	0.994	0.00728
	B	14	6.323	14.530	2.777	109.785	0.950	0.020
	C	14	7.171	21.741	1.424	110.800	0.9807	0.0128
11	A	14	−74.898	−7.755	0.549	205.012	0.996	0.00249
	B	14	5.284	12.741	2.064	128.319	0.945	0.0159
	C	14	5.886	19.173	1.132	129.227	0.984	0.00874
12	A	14	136.697	0.314	1.716	0.143	0.9998	0.0131
	B	14	4.338	11.384	1.879	135.149	0.941	0.0138
	C	14	4.670	17.067	1.022	135.949	0.983	0.00752
13	A	14	−41.992	−0.510	0.647	189.349	0.991	0.00441
	B	14	3.199	10.605	1.683	146.470	0.944	0.011
	C	14	3.598	15.295	1.154	147.04	0.9726	0.00786
14	A	14	−26.919	−0.454	1.055	163.015	0.979	0.00779
	B	14	4.388	10.470	1.841	134.516	0.937	0.0136
	C	14	5.058	15.264	1.818	135.101	0.952	0.0195
15	A	10	−99.123	−8.815	0.323	251.735	0.998	0.00213
	B	10	4.33	11.671	1.355	150.766	0.964	0.0089
	C	10	4.706	16.591	0.701	152.187	0.990	0.00462
16	A	9	28.896	−0.116	3.384	124.916	0.765	0.0222
	B	9	8.744	8.418	8.736	151.407	0.702	0.024
	C	9	3.856	10.533	4.104	152.375	0.624	0.027
17	A	8	56.405	0.145	0.097	65.711	0.999	0.000801
	B	8	1.495	4.447	0.707	121.233	0.947	0.00582
	C	8	1.414	5.751	1.029	121.670	0.885	0.00847
18	A	8	−21.092	−0.273	0.608	147.056	0.9798	0.00484
	B	8	3.587	5.013	0.584	124.360	0.981	0.00465
	C	8	4.142	7.534	0.570	125.055	0.982	0.0045
19	A	8	−11.718	−0.199	1.114	146.343	0.9101	0.00862
	B	8	1.971	5.370	0.750	133.813	0.960	0.00559
	C	8	1.999	6.863	1.232	134.32	0.888	0.00918
20	A	10	−112.065	−0.935	1.915	284.408	0.9994	0.00158
	B	10	5.035	13.008	1.474	120.04	0.967	0.0121
	C	10	5.134	19.427	0.756	121.880	0.9918	0.00624
21	A	5	45.167	−0.047	0.643	75.831	0.992	0.00541
	B	5	4.026	11.860	0.864	120.311	0.997	0.00806
	C	5	10.276	19.227	1.949	120.34	0.999	0.00163
22	A	5	−123.245	−0.964	0.105	275.880	0.9998	0.000704
	B	5	1.337	14.218	0.430	152.654	0.996	0.00288
	C	5	6.538	21.754	0.342	152.695	0.997	0.00229
23	A	5	−163.297	−1.235	0.144	294.433	0.9997	0.00112
	B	5	1.480	16.912	0.597	131.119	0.995	0.00469
	C	5	7.582	25.812	0.614	131.170	0.995	0.00482

(*Table 6 Contd.*)

24	A	8	−49.640	−0.580	0.205	186.803	0.9987	0.0015
	B	8	4.125	11.541	1.569	135.226	0.941	0.0106
	C	8	3.787	14.943	0.491	137.069	0.992	0.00366
25	A	11	−133.611	−1.116	0.394	272.501	0.999	0.00288
	B	11	9.251	12.579	3.069	134.40	0.981	0.0225
	C	11	6.914	22.615	1.049	137.620	0.991	0.00767
26	A	7	−123.482	−1.038	0.202	125.294	0.999	0.08898
	B	7	7.507	13.762	3.954	−0.944	0.794	0.760
	C	7	6.089	20.167	0.5184	1.808	0.996	0.0987
27	A	8	−211.057	−1.384	0.515	211.578	0.996	0.107
	B	8	6.859	11.562	3.709	−2.221	0.785	0.769
	C	8	4.717	19.355	0.969	0.887	0.986	0.2008
28	A	7	−59.388	−0.686	0.925	186.199	0.991	0.00741
	B	7	7.143	11.759	3.680	124.272	0.855	0.0294
	C	7	5.499	18.225	1.454	125.889	0.978	0.0116
29	A	6	−84.365	−0.795	0.649	236.349	0.995	0.00436
	B	6	3.323	13.261	1.919	150.128	0.959	0.0129
	C	6	3.500	20.210	1.269	151.978	0.982	0.0085
30	A	7	81.993	0.0412	0.462	89.917	0.997	0.00886
	B	7	3.659	14.294	1.620	121.207	0.965	0.0135
	C	7	8.521	17.460	2.422	120.494	0.920	0.020
31	A	7	−120.652	−0.880	0.288	277.068	0.998	0.00186
	B	7	1.227	18.081	0.826	156.849	0.986	0.0067
	C	7	3.197	15.871	0.59	156.62	0.991	0.0048
32	A	9	−117.318	−1.468	0.512	312.117	0.998	0.00888
	B	9	8.530	17.860	2.546	130.506	0.958	0.198
	C	9	9.785	28.965	1.01	133.427	0.991	0.0077
33	A	8	−221.875	−1.667	0.445	351.723	0.999	0.00356
	B	8	8.281	19.285	2.777	125.818	0.959	0.022
	C	8	8.781	18.701	0.634	128.774	0.998	0.0051
34	A	6	2098.345	11.154	2.547	−1969.484	0.994	0.020
	B	6	−12.477	−62.217	11.606	139.825	0.879	0.0911
	C	6	−8.884	−82.965	8.375	130.040	0.939	0.0658
35	A	10	−92.183	−0.816	0.247	229.517	0.998	0.001798
	B	10	4.860	13.523	1.871	135.094	0.954	0.0099
	C	10	4.477	16.937	0.416	137.078	0.996	0.0027
36	A	6	−87.744	−0.867	0.144	238.793	0.999	0.00103
	B	6	5.976	16.128	2.514	138.787	0.899	0.0175
	C	6	7.155	32.116	0.332	141.135	0.998	0.0024
37	A	7	−125.258	−1.01008	0.137	268 401	0.999	0.000966
	B	7	6.061	17.027	2.328	140.784	0.898	0.0168
	C	7	7.2r3	23.332	0.435	143.267	0.996	0.0081
38	A	9	−0.602	−0.271	0.501	153.07	0.992	0.0186
	B	9	7.711	6.207	3.268	150.425	0.806	0.0213
	C	9	10.317	7.807	3.702	151.08	0.742	0.0241
39	A	7	−78.049	−0.848	0.143	213.172	0.999	0.0011
	B	7	6.360	15.287	1.974	132.01	0.974	0.0148
	C	7	5.972	23.432	1.534	134.45	0.984	0.0115

References

1. L. P. HAMMETT, *J. Am. Chem. Soc.*, 1937, **59**, 96.
2. H. SPIESECKE and W. G. SCHNEIDER. *J. Chem. Phys.*, 1961, **35**, 781.
3. P. C. LAUTERBER, *Ann. N. Y. Acad. Sci.*, 1958, **70**, 841.
4. P. C. LAUTERBER, *J. Am. Chem. Soc.*, 1961, **83**, 1846.
5. S. EHRENSEN, R. T. C. BROWNLEE and R. W. TAFT, *Prog. Phys. Org. Chem.*, 1973, **10**, 1.
6. E. M. SCHULMAN, K. A. CHRISTENSEN, D. M. GRANT C. WALLING, *J. Org. Chem.*, 1974, **39**, 2686.
7. A. J. HOEFNAGEL, M. A. HOEFNAGEL and B. M. WEPSTER, *J. Org. Chem.*, 1978, **43**, 4720.
8. R. D. TOPSOM, *Prog. Phys. Org. Chem.*, 1976, **12**, 1.
9. J. BROMILOW, R. T. C. BROWNLEE, R. D. TOPSOM and R. W. TAFT, *J. Am. Chem. Soc.*, 1976, **98**, 2020.
10. W. J. HEHRE, R. W. TAFT and R. D. TOPSOM, *Prog. Phys. Org. Chem.*, 1976, **12**, 159.
11. C. G. SWAIN and E. C. LUPTON, *J. Am. Chem. Soc.*, 1968, **90**, 4328.
12. G. M. BODNER and L. J. TODD, *Inorg. Chem.*, 1974, **13**, 360.
13. D. R. COULSON, *J. Am. Chem. Soc.*, 1976, **98**, 311.
14. M. GODFREY, *J. Chem. Soc., Perkin Trans.* 2, 1977, 769.
15. F. HRUSKA, H. M. HUTTON and T. SCHAEFER, *Can. J. Chem.*, 1965, **43**, 2392.
16. W. B. SMITH, A. M. IHRIG and J. I. ROARK, *J. Phys. Chem.*, 1970, **74**, 812.
17. M. J. S. DEWAR, R. GOLDEN and J. M. HARRIS, *J. Am. Chem. Soc.*, 1971, **93**, 4187.
18. D. A. DAWSON and W. F. REYNOLDS, *Can. J. Chem.*, 1975, **53**, 373.
19. W. F. REYNOLD and G. K. HAMER, *J. Am. Chem. Soc.*, 1976, **98**, 7296.
20. J. BROMILOW, R. T. C. BROWNLEE, D. J. CRAIK, M. SADEK and R. W. TAFT, *J. Org. Chem.*, 1980, **45**, 2419.
21. S. N. SAWHNEY and D. W. BOYKIN, *J. Org. Chem.*, 1979, **44**, 1137.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 996-997

Syntheses of 3-Bromochromones

A. K. D. MAZUMDAR, G. C. SAHA, T. K. SINHA and K. D. BANERJI*

Chemical Laboratory, Bhagalpur University, Bhagalpur-812 007

Fifteen 3-bromochromones have been prepared by brominating the corresponding hydroxyaroyl aroyl/heteroyl methanes and cyclization. Direct bromination of chromones to yield 3-bromochromones has been studied by three different reagents, (i) bromine, (ii) *N*-bromosuccinimide and (iii) cupric bromide. Cupric bromide gives the best result. The chromone structures have been established by analysis, spectral data and their conversion to the corresponding coumaran-3-ones.

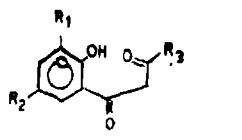
BROMINATION of chromones using bromine in different solvents produce 3-bromochromones but the products are contaminated with other derivatives and the yields are not very satisfactory. Prior to 1978, *N*-bromosuccinimide has been used to brominate 2-methylchromones by two sets of workers[1,2]. A reinvestigation by Rastogi *et al.*[3] showed that the 3-bromochromone is the major product and two other isomeric compounds are often simultaneously produced. Wadodkar and Doifode[4] have recently converted 2-hydroxybenzoylbenzoylmethanes into 3-bromochromones by brominating the diketones using molecular bromine and dioxane when the intermediate bromo derivatives get directly converted into 3-bromochromones.

Since these authors have used only six diketones of the type $R_1COCH_2COR_2$ (where R_1 and R_2 are both benzenoid) it was cosidered worthwhile to investigate if the route is of general application. For the purpose five diketones were chosen, where R_1 and R_2 are both aromatic, while in ten others the R_2 moiety is either furyl or thineyl (Chart 1)

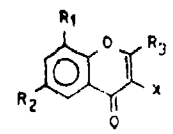
All the fifteen diketones I (a-o) were brominated with bromine in dioxane at room temperature and gave the corresponding 3-bromochromones, II (a-o), in 60-80% yield. All the 3-bromochromones were analysed correctly for carbon and hydrogen. The 3-bromochromones, on refluxing with alcoholic KOH, easily gave the 2-aroyl (III, a-e) or 2-heteroyl (III, f-o) coumaran-3-ones.

The coumaran-3-ones (III) were found to be identical with samples prepared by earlier workers[5,6] in this laboratory and whose structures had thoroughly been established by elemental analysis, chemical properties, ir and pmr data. Chromones and their heterocyclic analogues invariably show signal[7] for the proton at 3-position δ 6.63-6.67, which is indeed characteristic of chromones. In the 3-bromochromones this proton signal was missing, thus confirming the structure of 3-bromochromones.

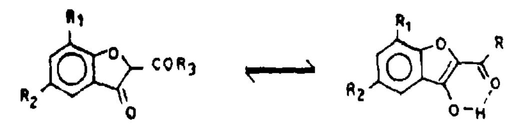
The study was extended to find how far it was possible to prepare satisfactorily 3-bromo derivatives directly from the chromones or their heterocyclic analogues. The latter set of compounds are prone to substitution by bromine while in chromones the



I



II, X = Br;
IV, X = H.



III

Chart 1

a $R_1 = CH_3$, $R_2 = Br$, $R_3 = 4'$-Bromophenyl
b $R_1 = H$, $R_2 = CH_3$, $R_3 = 4'$-Bromophenyl
c $R_1 = Br$, $R_2 = CH_3$, $R_3 = 4'$-Bromophenyl
d $R_1 = H$, $R_2 = Cl$, $R_3 = 4'$-Bromophenyl
e $R_1 = Br$, $R_2 = Cl$, $R_3 = 4'$-Bromophenyl
f $R_1 = CH_3$, $R_2 = Br$, $R_3 = 2$-Furyl
g $R_1 = H$, $R_2 = CH_3$, $R_3 = 2$-Furyl
h $R_1 = Br$, $R_2 = CH_3$, $R_3 = 2$-Furyl
i $R_1 = H$, $R_2 = Cl$, $R_3 = 2$-Furyl
j $R_1 = Br$, $R_2 = Cl$, $R_3 = 2$-Furyl
k $R_1 = CH_3$, $R_2 = Br$, $R_3 = 2$-Thienyl
l $R_1 = H$, $R_2 = CH_3$, $R_3 = 2$-Thienyl
m $R_1 = Br$, $R_2 = CH_3$, $R_3 = 2$-Thienyl
n $R_1 = H$, $R_2 = Cl$, $R_3 = 2$-Thienyl
o $R_1 = Br$, $R_2 = Cl$, $R_3 = 2$-Thienyl

substituent in benzenoid ring at 2-position may affect the course of bromination. Bromination of fifteen chromones (IV, a-o), therefore, was undertaken and the substituent at 2-position was varied from phenyl to furyl to thienyl. Three brominating agents were used, namely (i) bromine in acetic acid, (ii) NBS in chloroform and (iii) cupric bromide.

Bromination using bromine invariably gave products which were gummy masses and from which crystals were difficult to obtain. This route, therefore, did not seem to be of much use from preparative point of view and was not investigated further.

Bromination by NBS gave the bromo derivatives in 50-70% yield, except in the case of 8-methyl-6-bromo-2-(2'-furyl)chromone, where the yield was *ca* 40%.

Cupric bromide has been used as a brominating agent in this laboratory and elsewhere[8], for brominating hydroxyacetophenones, coumarins[9] with good results but the reagent has not so far been used in this area. Addition of chromones, **IV(a-o)** to a refluxing solution of cupric bromide in dry ethyl acetate-chloroform and continuation of refluxing for several hours gave the 3-bromochromones in 50-80% yield. However, if a furan ring is present at 2-position of the chromone the yield is generally lower (*ca* 40%). In the pmr spectra, the chromone protons at 3-position show in the region δ 6.63 to 6.68, the furyl protons in the region 6.60 to 7.61, the thienyl protons in the region 7.15 to 7.75 and the benzenoid protons in the region 7.40 to 8.10.

Experimental

Melting points were recorded in open capillary and are uncorrected. The ir spectra were recorded in Beckman IR-20 spectrophotometer, using KBr or nujol mull.

3-Bromochromones (II) : (Procedure A). The diketone[7] (**I**, 0.01 mol) was dissolved in anhydrous dioxane (20 ml) and molecular bromine (0.05 ml) was added to the stirred solution in drops. Stirring was continued for 3 h. The reaction mixture on pouring in a large volume of water yielded a white precipitate, which was filtered, washed and crystallised from suitable solvent (Table 1).

Preparation of 3-bromochromones (**II**) *by bromination of chromones* **IV** *:* (Procedure B). To a solution of chromone **IV**[7] (0.01 mol) in chloroform (25 ml), *N*-bromosuccinimide (0.01 mol) was added. The mixture was refluxed for 12 h. A further amount of NBS (0.004 mol) was added over a period of 4 h, followed by refluxing for another 20 h. The mixture was then filtered and concentrated. The crystals, thus obtained, were filtered, washed and recrystallised (Table 1).

Procedure C : To a solution of cupric bromide (1 g) in ethyl acetate-chloroform mixture (2 : 1) was added chromone **IV(a-o)** (0.3 mol) and the solution was refluxed for 4-12 h. The grey-white precipitate of cuprous bromide, thus obtained, was filtered and the filtrate was evaporated to dryness. The solid residue, thus obtained, was crystallised. In some cases, a gummy mass was obtained which was extracted with benzene and passed over silica gel. The resulting solution was evaporated to dryness and the residue was crystallised (Table 1).

TABLE 1—3-BROMOCHROMONES (II)*

Compd. no.	M.p. °C	Solvent of crystallisation	Yield % A	Yield % B	Yield % C
a	171-72	Acetic acid	70	60	62
b	198-99	Acetic acid	76	70	75
c	211-12	Acetic acid	75	75	81
d	191-92	Acetic acid	78	70	76
e	198	Acetic acid	88	78	80
f	168-64	Acetic acid	68	49	42
g	188	Ethanol	69	58	50
h	193-95	Methanol	65	62	52
i	174-75	Methanol	62	60	55
j	148-49	Methanol	72	61	56
k	198-99	Ethanol	62	58	60
l	246-47	Ethanol	68	68	68
m	268-69	Ethanol	72	72	65
n	198-99	Ethanol	65	65	75
o	268-69	Ethanol	76	76	72

* Satisfactory C and H analyses, ν_{max} 1625-1645 cm^{-1} (C=O).

Preparation of 2-aroyl- or 2-heteroyl-coumaran-3-ones (III)[5,6] : A 3-bromochromone **II(a-o)** (0.01 mol) was dissolved in ethanol (30 ml) and ethanolic KOH (10 ml, 25%) was added to it. The mixture was gently refluxed for 2 h. The solution was then poured over ice-cold HCl (2 *N*). The solid, thus obtained, was filtered, washed and crystallised. The yields of **III(a-o)** were in the range of 70-90%.

Acknowledgement

The authors express their deep sense of indebtedness to Prof. J. N. Chatterjea, Patna University for his valuable suggestion and fruitful discussion and to the authorities of Bhagalpur University for facilities.

References

1. C. W. WINTER and C. S. HAMILTON, *J. Am. Chem. Soc.*, 1952, **74**, 3999.
2. P. F. WILEY, *J. Am. Chem. Soc.*, 1952, **74**, 4326.
3. M. K. RASTOGI, K. CHAUDHURY, R. P. KAPOOR and C. P. GARG, *Indian J. Chem., Sect. B*, 1978, **16**, 895.
4. P. N. WADODKAR and K. B. DOIFODE, *Indian J. Chem., Sect. B*, 1979, **18**, 458.
5. D. P. SARBAGGYA, A. K. D. MAZUMDAR and K. D. BANERJI, *Natl. Acad. Sci. letters*, 1979, **2**, 219.
6. K. RANGACHARI, A. K. D. MAZUMDAR and K. D. BANERJI, *J. Indian Chem. Soc.*, 1980, **57**, 1014.
7. D. P. SARBAGGYA, K. RANGACHARI, A. K. D. MAZUMDAR and K. D. BANERJI, *J. Indian Chem. Soc.*, 1981, **58**, 196.
8. K. B. DOIFODE and M. G. MARATHEY, *J. Org. Chem.*, 1964, **29**, 2025.
9. M. L. MALIK and S. K. GROVER, *Indian J. Chem., Sect. B*, 1976, **14**, 513.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 998-1006

Kinetics of Vapour Phase Oxidation of 1-Phenylethanol over Ferric Molybdate Catalyst

NARAYANASWAMY SUNDARARAMAN†, M. VIVEKANANDA BHATT†* and M. RAVINDRAM**

Indian Institute of Science, Bangalore-560 012

Kinetics of the vapour phase oxidation of 1-phenylethanol over ferric molybdate was studied in an isothermal, differential, fixed-bed reactor in the temperature range 240-300°. The sole product obtained was acetophenone. Twentyfour different models including redox, Langmuir-Hinshelwood and Rideal were examined to fit the experimental data. These models were compared and the redox model was found to be more satisfactory than the others.

CHEMISTRY of the catalytic processes, employed in industry are poorly understood. Also many of them bear little similarity to the methods used for preparing the same chemicals in the organic chemical laboratory.

Hoping that some of the well tested methods of physical organic chemistry could be applied for the study of heterogeneous catalytic reactions we started the present programme of work. In the study of catalytic reactions the emphasis is on the processes taking place on the surface of the catalyst. We thought we could focus our attention on the substrate and the detailed transformations it was going through before being converted to the product. We hope that it would lead to a deeper understanding of the chemical processes involved and possibly also throw light on some of the features of interaction between the substrate and the catalyst.

Oxidation of alcohols under homogeneous conditions is well studied. The mechanism of oxidation by a number of reagents like chromic acid, hypobromous acid, single electron oxidants like Ce^{IV} nitrate, *etc.*, has been fairly well understood.

One could write at least three distinct possibilities.

(i) Alcohol + Oxidant (acid) ⟶ decomposition

Ester — base ⟶ cyclic transition state / conjugate base ⟶ Carbonyl compound

(ii) Alcohol + Oxidant ⟶ Complex ⟶ Carbonyl compound.

(iii) Alcohol + Oxidant ⟶ Cation radical $\xrightarrow{-H^+}$ radical $\xrightarrow{\text{oxidation}}$ cation $\xrightarrow{-H^+}$ carbonyl compound.

In the present study of which this paper forms a part, we have examined the oxidation of 1-phenylethyl alcohols over ferric molybdate which is a selective catalyst for the vapour phase oxidation of aliphatic alcohols to carbonyl compounds[1-6].

Experimental

Apparatus, materials and methods : An all-glass apparatus consisting mainly of alcohol mixer, preheater, reactor and product collection unit (a series of bubblers and double surface condensers) was used. A schematic diagram of the apparatus used is shown in Fig. 1. The reactor (30 cm × 2 cm dia.) had a perforated glass plate as catalyst support. Heating was accomplished in all cases with externally wound Kanthal (nichrome resistance) heating wire. The power input to the system at various points in the set-up was controlled by variable auto-transformers and simmerstats and the temperature was measured by a calibrated chromel-alumel thermocouple.

The materials consisted of distilled 1-phenylethanol (Fluka, A.G.), nitrogen of purity 99% in cylinder (Indian Oxygen) and air. Nitrogen and air drawn from the compressed air line were purified from the entrained oil, moisture and carbon dioxide. The gases were metered at ambient conditions of 0.899 std. atm and 25°. The ferric molybdate catalyst was prepared from ferric nitrate and ammonium paramolybdate as described by Kolovertnov *et al*[7]. The physical properties of the catalyst are listed in Table 1.

A known amount of the catalyst contained in the reactor was first purged with nitrogen at the desired temperature. Vapours of alcohols were oxidised over the catalyst in the reactor in a current of air and nitrogen. Samples were collected for analysis when the catalyst bed temperature had remained constant and steady state was reached. The only

† Department of Organic Chemistry.

** Department of Chemical Engineering.

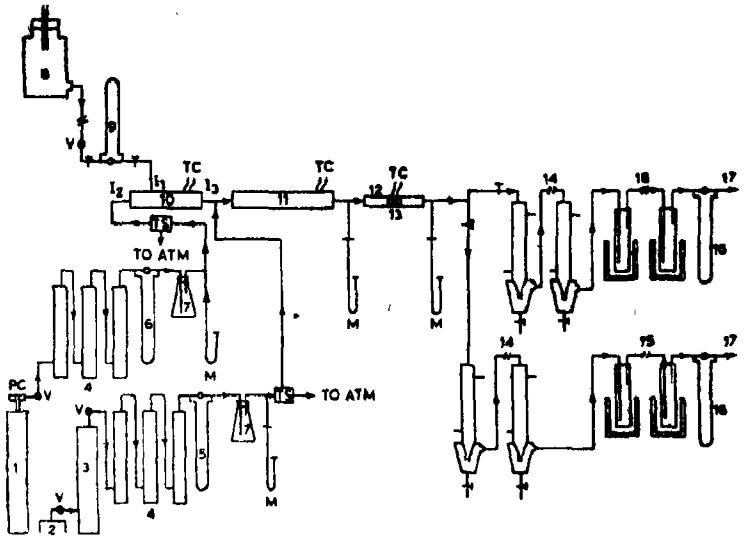


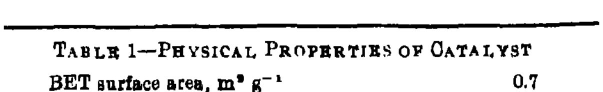
Fig. 1. Flow diagram. Experimental set up.
1 Nitrogen cylinder, 2 Compressed air reservoir, 3 Pressure compensating drum, 4 Air and nitrogen purifying towers, 5 Capillary flow meter for air, 6 Capillary flow meter for nitrogen, 7 Manometric fluid collector, 8 Alcohol reservoir, 9 Capillary flow meter for alcohol, 10 Mixer, 11 Preheater, 12 Reactor, 13 Catalyst bed, 14 Condenser cum bubbler train, 15 Ice cooled absorber train, 16 Capillary flow meter for vent gas, 17 To gas sampler, 18 Pressure control valve, V Needle valve, T Two-way stop cock, TS Three-way stop cock, M Manometer, TC Thermocouple, I1 Inlet for alcohol, I2 Inlet for nitrogen, I3, Inlet for air.

TABLE 1—PHYSICAL PROPERTIES OF CATALYST

BET surface area, $m^2 g^{-1}$	0.7
Average particle diameter, μ	192
Bulk density, $g\ cm^{-3}$	1.55
Particle density, $g\ cm^{-3}$	3.5
Pore volume, $cm^3 g^{-1}$	0.025
Average pore radius, Å	714

eaction product acetophenone was confirmed by lc and spectroscopic analyses. An Orsat gas analysis of the exit gas indicated that the amounts of carbon ioxide and carbon monoxide formed were insigni- icant. The product acetophenone was quantitatively stimated by measuring the intensity of the colour f its complex with 2,4-dinitrophenylhydrazine[8]. 'he amount of unreacted 1-phenylethanol was stimated similarly by complexing with ceric mmonium nitrate[9]. The effects of partial pressures f alcohol and oxygen on the rate of reaction are ıbulated in Tables 2 and 3.

Before carrying out preliminary studies, a ıermodynamic analysis of the reaction under :udy, *i.e.*



:vealed the irreversible nature of the reaction as at)0° the equilibrium constant is 4.8×10^{21}.

Diffusion effects : Experiments were conducted ı find the regions in which resistance due to physical transport phenomena (inter- and intra-phase mass diffusion) do not influence the reaction rate. It was found that above a feed flow rate of 200 l h^{-1} the effect of interphase diffusion on reaction rate was insignificant and with catalyst particle size of 440 μ and lower intraphase diffusion rate did not influence the reaction rate. The results are depicted in Figs. 2 and 3. In the actual kinetic runs, feed flow rates of the order of 400 l h^{-1} and catalyst particle size of 192 μ were employed. The effect of time factor and life of the catalyst on conversion is shown in Figs. 4 and 5. The influence of interphase diffusion was tested by the method of Yoshida *et al.*[10] corresponding to the values of the following variables at 300°.

Modified Reynolds no. (Re) = 0.47
Schmidt no. (Sc) = 2.17
Rate no. (R) = 2.60×10^{-8}

The ratio of partial pressure difference of reactant between bulk phase and catalyst surface to the partial pressure in the bulk phase was found to be 1.14×10^{-5} indicating the absence of external diffusional effects. The intraparticle diffusional effect was checked by Weisz and Hick's method[11]. For the Thiele type modulus of 0.15, the effectiveness factor is unity and this shows the insignificant nature of intraparticle diffusion.

Kinetic analysis : The conversion in most cases was below 11% except at the maximum temperature of 300°. The error involved in assuming differential reactor analysis was found[2,3] to be 1%. The initial

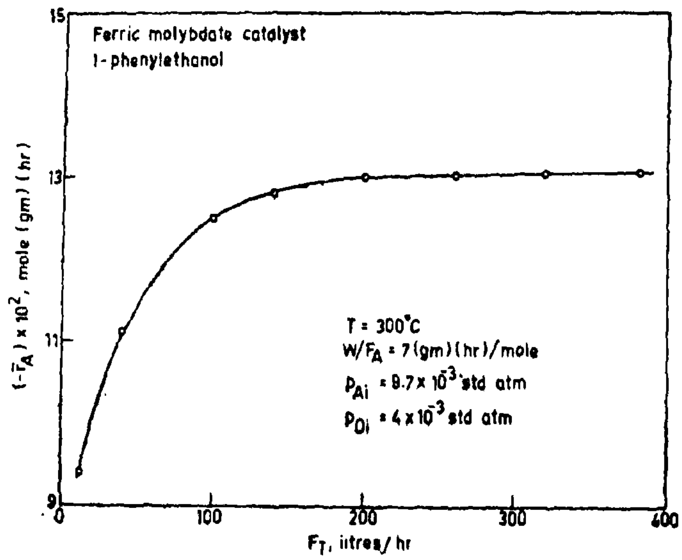


Fig. 2. Effect of external diffusion.

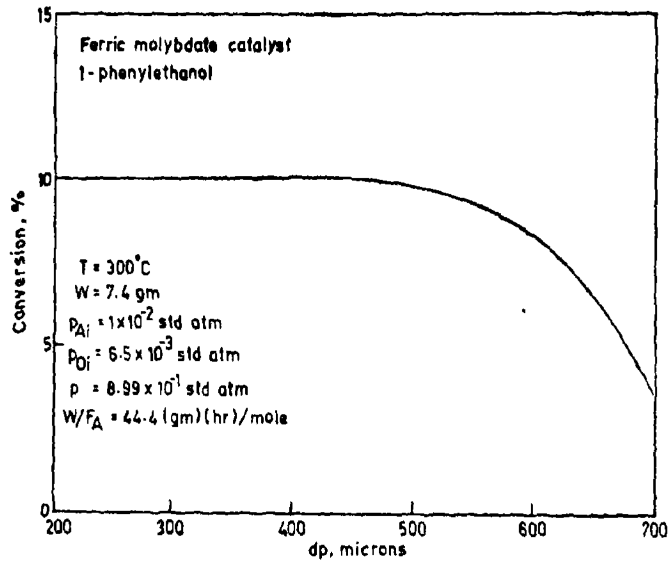


Fig. 3. Effect of internal diffusion.

rates were calculated using the approximate equation (1).

$$\text{Initial rate} = [\text{mean rate}] \times \frac{[\text{initial conc. of reactant}]}{[\text{mean conc. of reactant}]} \quad (1)$$

As θ, the relative concentration of surface oxygen taking part in both the stages of redox model, is fairly constant in the experimental conditions covered, the use of equation (1) in calculating the initial rate is justified. The initial rates thus calculated were compared with the experimental rates and it was found that the overall deviation was less than 6%. The above analysis gives a good justification for using a differential reactor analysis. The rate equation for the analysis of the data can be expressed as

$$-r_A = dx_A/d[W/F_A] \quad (2)$$

Results and Discussion

Recent literature on vapour phase oxidation using transition metal oxides as catalysts has shown that a redox mechanism operates in a number of cases[13-15]. According to this model the oxidation proceeds by simultaneous reduction of the catalyst

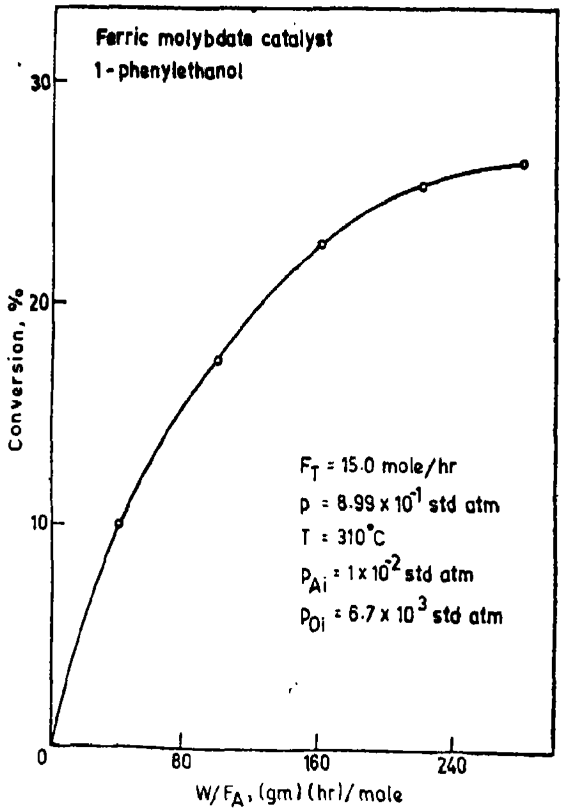


Fig. 4. Effect of time-factor on conversion.

surface by the reactant and reoxidation by oxygen in the bulk phase. The mechanism can be represented as

$$\text{reactant} + C_{-ox} \xrightarrow{k_A} \text{products} + C_{-red}$$

$$O_2 + C_{-red} \xrightarrow{k_O} C_{-ox}$$

where C_{-ox} and C_{-red} represent the oxidised and reduced forms of the catalyst, respectively. The rate equation based on the above mechanism adapted to the present system can be given as

$$-r_A = \frac{k_A k_O p_A^m p_O^n}{k_O p_O^n + N k_A p_A^m} \qquad (3)$$

Experiments were planned to test the redox model. The runs were conducted in a steady state isothermal flow reactor. Tables 2 and 3 show typical data along with the experimental rates. The two-stage redox equation (3) was coupled with the mass

TABLE 2—EFFECT OF PARTIAL PRESSURE OF ALCOHOL ON RATE AT CONSTANT OXYGEN PARTIAL PRESSURE*

Temp. °C	Initial alcohol partial pressure, std. atm	Time factor (g)(h)mol^{-1}	Conversion %	Rate $\times 10^4$(mol/h)(g)
240	0.0028	166.70	1.77	1.06
	0.0060	77.81	1.71	2.21
	0.0090	51.41	1.66	3.22
	0.0100	44.35	1.57	3.54
255	0.0028	166.92	2.92	1.75
	0.0060	77.31	2.81	3.64
	0.0090	51.38	2.73	5.32
	0.0100	44.44	2.60	5.85
270	0.0028	166.74	4.65	2.79
	0.0060	77.42	4.51	5.82
	0.0090	51.44	4.38	8.51
	0.0100	44.35	4.16	9.38
285	0.0028	166.18	7.21	4.34
	0.0060	77.65	7.04	9.06
	0.0090	51.54	6.84	13.30
	0.0100	44.37	6.50	14.60
300	0.0028	166.40	10.78	6.48
	0.0060	77.58	10.54	13.60
	0.0090	51.49	10.28	20.00
	0.0100	44.42	9.79	22.00

* Catalyst : ferric molybdate ; oxygen partial pressure : 0.0068 std. atm ; total flow rate : 300 l h^{-1} ; total pressure : 0.899 std. atm.

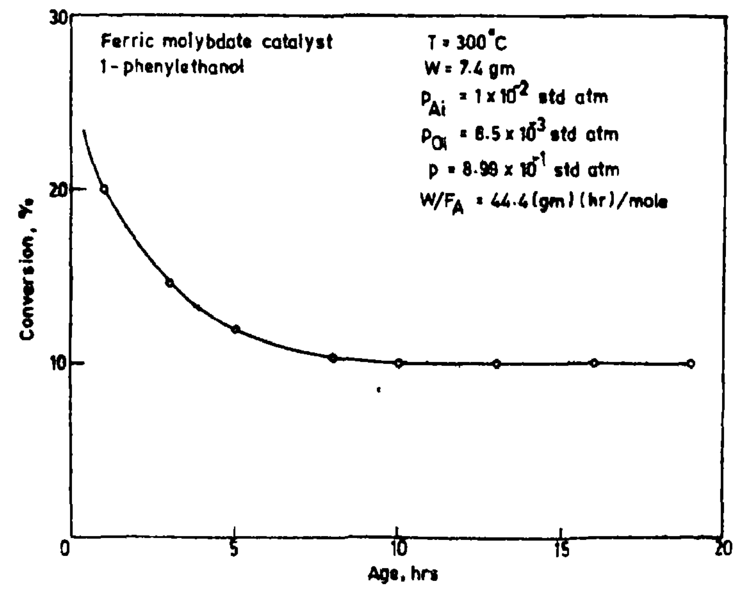


Fig. 5. Effect of life of catalyst on conversion.

TABLE 3—EFFECT OF PARTIAL PRESSURE OF OXYGEN ON RATE AT CONSTANT ALCOHOL PARTIAL PRESSURE*

Temp. °C	Initial oxygen partial pressure, std. atm	Time factor (g)(h)mol⁻¹	Conversion %	Rate $\times 10^4$(mol/h)(g)
240	0.0045	77.95	1.79	2.29
	0.0026	77.22	1.72	2.23
	0.0014	77.89	1.67	2.15
	0.0007	77.82	1.58	2.03
255	0.0045	77.74	2.94	3.78
	0.0026	77.49	2.86	3.69
	0.0014	77.66	2.76	3.56
	0.0007	77.58	2.61	3.36
270	0.0045	77.55	4.69	6.05
	0.0026	77.65	4.58	5.90
	0.0014	77.47	4.42	5.71
	0.0007	77.58	4.19	5.40
285	0.0045	77.56	7.31	9.43
	0.0026	77.53	7.14	9.21
	0.0014	77.48	6.90	8.91
	0.0007	77.49	6.52	8.42
300	0.0045	77.59	10.96	14.1
	0.0026	77.56	10.73	13.8
	0.0014	77.57	10.39	13.4
	0.0007	77.49	9.81	12.7

* Catalyst : ferric molybdate ; alcohol partial pressure : 0.0063 std. atm ; total flow rate : 300 l·h⁻¹ ; total pressure : 0.899 std. atm.

conservation equation (2), and was integrated for four combinations of reaction orders m and n, *viz.* [1, 1], [0.5, 1], [0.5, 0.5] and [1, 0.5]. The four integrated rate equations can be written as

$$-1/\bar{r}_A = 1k_A\bar{p}_A + N/k_O\bar{p}_O \qquad (4)$$

for $m = n = 1$

$$\bar{p}_A = \frac{p_{Ai} - p_{Af}}{\ln[p_{Ai}/p_{Af}]} \qquad (5)$$

$$\bar{p}_O = \frac{p_{Oi} - p_{Of}}{\ln[p_{Oi}/p_{Of}]} \qquad (6)$$

for $m = n = 0.5$

$$\bar{p}_A = \frac{p_{Ai}^{0.5} + p_{Af}^{0.5}}{2} \qquad (7)$$

$$\bar{p}_O = \frac{p_{Oi}^{0.5} + p_{Of}^{0.5}}{2} \qquad (8)$$

where $p_{Af} = p_{Ai}[1 - x_A]$, and $p_{Of} = p_{Oi} - Np_{Ai}x_A$.

Along with the redox model, some other models were also tested for their validity for the present system. These are listed in Table 4. Initial rate data were used for testing these models. The parameters were estimated from the linearised equations of the models using the method of least squares. The parameters of the models thus estimated are included in Table 5.

Comparison of various models : For distinguishing among the different models use is made of the following criteria.

(i) Since all constants represent some chemical process they should have positive values to satisfy physical reality.

(ii) All constants should exhibit temperature sensitivity and be capable of being fitted to an Arrhenius type equation from which activation energies of reaction, adsorption, *etc.*, can be evaluated.

(iii) A given model should give a good fit to the experimental data.

The models were evaluated using these criteria and the conclusions drawn are summarised in Table 6. It was found that only the two-stage redox models with order combinations [1, 1 ; model 1] and [1, 0.5 ; model 4] satisfy all the criteria. Therefore, all other models were rejected.

TABLE 4—MODELS OTHER THAN TWO STAGE REDOX MODEL TESTED FOR 1-PHENYLETHANOL OXIDATION

Model no*	Model	Model equation
5-8	Steady state adsorption model with additional assumption that the oxygen desorption rate is not negligible	$-r_A = \frac{k_A k'_O p_A^m p_O^n}{Nk_A p_A^m + k'_O p_O^n + k_d}$
9-12	Rideal model	$-r_A = \frac{kK_O p_O^n p_A^m}{1 + K_O p_O^n}$
13-16	Langmuir Hinshelwood model (surface reaction controlling)	$-r_A = \frac{kK_A K_O p_O^n p_O^m}{[1 + k_O p_O^n + k_A p_A^m]^2}$
17-20	Langmuir Hinshelwood model (surface reaction controlling, oxygen dissociatively adsorbed)	$-r_A = \frac{kK_A p_A^m \sqrt{K_O p_O^n}}{[1 + K_A p_A^m + \sqrt{K_O p_O^n}]^2}$
21-24	Empirical model	$-r_A = kp_A^m p_O^n$

* Under each category the four models are respectively, where m = 1, n = 1 ; m = 0.5, n = 1 ; m = 0.5, n = 0.5 and m = 1, n = 0.5.

TABLE 5—CONSTANTS OF VARIOUS MODELS BASED ON INITIAL RATE

Model no.	Temp. °C	Values of parameters			Av. abs. devn.
		k_A	k_O		
1	240	3.84 E−2*	8.16 E−1		6.32 E 0
	255	6.87 E−2	1.38 E 0		8.67 E 0
	270	1.03 E−1	2.32 E 0		8.35 E 0
	285	1.62 E−1	3.70 E 0		6.59 E 0
	300	2.47 E−1	5.85 E 0		7.77 E 0
2	240	1.61 E−4	−2.50 E−2		1.47 E+1
	255	2.67 E−4	−4.10 E−2		1.38 E+1
	270	4.28 E−4	−6.46 E−2		2.34 E+1
	285	6.70 E−4	−1.01 E−1		3.24 E+1
	300	1.01 E−3	−1.50 E−1		1.51 E+1
3	240	1.31 E−4	−3.30 E−4		1.53 E+1
	255	2.16 E−4	−5.45 E−4		2.81 E+1
	270	3.46 E−4	−8.63 E−4		2.42 E+1
	285	5.41 E−4	−1.35 E−3		1.78 E+1
	300	8.16 E−4	−2.01 E−3		1.77 E+1
4	240	3.99 E−2	2.03 E−2		8.25 E−2
	255	6.62 E−2	3.42 E−2		5.06 E−2
	270	1.06 E−1	5.78 E−2		2.87 E−2
	285	1.68 E−1	9.26 E−2		2.66 E−2
	300	2.55 E−1	1.48 E−1		3.39 E−2
		k_A	k'_O	$k_A k'_O/k_d$	
5	240	3.76 E−2	2.36 E−1	−9.90 E+1	2.05 E 0
	255	6.25 E−2	3.93 E−1	−1.63 E+2	2.07 E 0
	270	1.01 E−1	6.72 E−1	−2.81 E+2	2.52 E 0
	285	1.59 E−1	1.11 E 0	−4.72 E+2	1.94 E 0
	300	2.13 E−1	1.88 E 0	−8.24 E+2	1.82 E 0
6	240	2.02 E−4	−4.81 E−4	1.21 E−2	1.55 E+1
	255	3.34 E−4	−7.96 E−4	2.01 E−4	1.56 E+1
	270	5.36 E−4	−1.27 E−3	3.21 E−2	1.57 E+1
	285	8.41 E−4	−1.99 E−3	5.01 E−2	1.61 E+1
	300	1.27 E−3	−2.99 E−3	7.54 E−2	1.61 E+1
7	240	1.96 E−4	−3.97 E−5	1.01 E−3	1.49 E+1
	255	3.24 E−4	−6.58 E−5	1.68 E−3	1.49 E+1
	270	5.18 E−4	−1.05 E−4	2.69 E−3	1.50 E+1
	285	8.11 E−4	−1.64 E−4	4.19 E−3	1.51 E+1
	300	1.22 E−3	−2.47 E−4	6.31 E−3	1.54 E+1
8	240	4.00 E−2	2.13 E−2	9.60 E+1	3.55 E 0
	255	6.63 E−2	3.53 E−2	2.63 E+2	4.41 E 0
	270	1.07 E−1	6.05 E−2	2.93 E+2	3.57 E 0
	285	1.68 E−1	1.00 E−1	2.74 E+2	1.47 E 0
	300	2.57 E−1	1.71 E−1	2.49 E+2	2.15 E 0
		k	kK_O		
9	240	3.86 E−2	2.56 E+2		2.70 E+1
	255	6.40 E−2	4.33 E+2		2.67 E+1
	270	1.03 E−1	7.28 E+2		2.52 E+1
	285	1.63 E−1	1.16 E+3		2.41 E+1
	300	2.48 E−1	1.82 E+3		2.35 E+1
10	240	1.64 E−4	−7.99 E−1		3.15 E+1
	255	2.72 E−4	−1.13 E 0		3.13 E+1
	270	4.36 E−4	−2.06 E 0		3.38 E+1
	285	6.84 E−4	−3.21 E 0		3.20 E+1
	300	1.03 E−3	−4.76 E 0		3.41 E+1
11	240	1.46 E−4	−1.43 E−2		3.57 E+1
	255	2.42 E−4	−2.85 E−2		3.65 E+1
	270	3.87 E−4	−3.69 E−2		3.86 E+1
	285	6.06 E−4	−5.76 E−2		3.83 E+1
	300	9.13 E−4	−8.57 E−2		3.77 E+1
12	240	4.15 E−2	5.29 E 0		2.29 E+1
	255	6.88 E−2	8.96 E 0		2.27 E+1
	270	1.10 E−1	1.51 E+1		1.79 E+1
	285	1.74 E−1	2.40 E+1		2.13 E+1
	300	2.64 E−1	3.80 E+1		2.01 E+1

(Table 5 contd.)

Model no.	Temp. °C	Values of parameters			Av. abs. devn.
		$(kK_A K_O)^{0.5}$	$(kK_O/K_A)^{0.5}$	$(kK_A/K_O)^{0.5}$	
13	240	9.40 E 0	3.03 E−1	2.19 E−2	1.17 E+1
	255	1.21 E+1	3.91 E−1	2.81 E−2	1.05 E+1
	270	1.54 E+1	5.16 E−1	3.57 E−2	1.29 E+1
	285	1.92 E+1	6.68 E−1	4.48 E−2	1.33 E+1
	300	2.35 E+1	8.80 E−1	5.54 E−2	1.14 E+1
14	240	1.30 E−1	−1.29 E−2	1.53 E−3	1.22 E+1
	255	1.67 E−1	−1.65 E−2	2.03 E−3	1.34 E+1
	270	2.11 E−1	−2.09 E−2	2.57 E−3	1.42 E+1
	285	2.63 E−1	−2.61 E−2	3.22 E−3	1.25 E+1
	300	3.22 E−1	−3.19 E−2	3.96 E−3	1.37 E+1
15	240	3.42 E−2	−3.65 E−3	6.57 E−3	4.74 E 0
	255	3.41 E−2	−4.49 E−3	8.44 E−3	3.26 E 0
	270	5.58 E−2	−5.92 E−3	1.07 E−2	3.76 E 0
	285	6.97 E−2	−7.39 E−3	1.33 E−2	1.57 E 0
	300	8.55 E−2	−9.04 E−3	1.64 E−2	1.03 E 0
		$(kK_A K_O)^{0.5}$	$(kK_O/K_A)^{0.5}$	$(kK_A/K_O)^{0.5}$	
16	240	1.68 E 0	1.14 E−1	9.72 E−2	3.51 E 0
	255	2.17 E 0	1.47 E−1	1.25 E−1	3.75 E 0
	270	2.76 E 0	1.97 E−1	1.58 E−1	3.38 E 0
	285	3.46 E 0	2.57 E−1	1.98 E−1	3.91 E 0
	300	4.26 E 0	3.46 E−1	2.45 E−1	3.23 E 0
		$(kK_A)^{0.5} \times (K_O)^{0.25}$	$(k/K_A)^{0.5} \times (K_O)^{0.25}$	$(kK_A)^{0.5}/(K_O)^{0.25}$	
17	Numerically corresponds to model 16 rate constant combinations.				
18	Numerically corresponds to model 15 rate constant combinations.				
19	240	1.77 E−2	−1.95 E−3	1.35 E−2	9.57 E 0
	255	2.28 E−2	−2.50 E−3	1.73 E−2	9.53 E 0
	270	2.89 E−2	−3.16 E−3	2.17 E−2	9.47 E 0
	285	3.61 E−2	−3.95 E−3	2.72 E−2	9.42 E 0
	300	4.43 E−2	−4.83 E−3	3.32 E−2	9.63 E 0
20	240	6.83 E−1	6.69 E−2	2.33 E−1	4.63 E 0
	255	6.91 E−1	8.64 E−2	2.98 E−1	4.54 E 0
	270	1.14 E 0	1.16 E−1	3.75 E−1	4.33 E 0
	285	1.43 E 0	1.52 E−1	4.70 E−1	3.64 E 0
	300	1.76 E 0	2.07 E−1	5.78 E−1	4.21 E 0
		k			
21	240	1.01 E+1			6.60 E+1
	255	1.68 E+1			6.61 E+1
	270	2.71 E+1			6.62 E+1
	285	4.28 E+1			6.63 E+1
	300	6.54 E+1			6.64 E+1
22	240	6.30 E−2			7.90 E+1
	255	1.04 E−1			7.92 E+1
	270	1.68 E−1			7.94 E+1
	285	2.64 E−1			7.95 E+1
	300	3.99 E−1			7.98 E+1
23	240	3.75 E−3			4.45 E+1
	255	6.22 E−3			4.46 E+1
	270	9.99 E−3			4.48 E+1
	285	1.57 E−2			4.50 E+1
	300	2.38 E−2			4.53 E+1
24	240	6.01 E−1			3.06 E+1
	255	9.98 E−1			3.07 E+1
	270	1.61 E 0			3.08 E+1
	285	2.55 E 0			3.08 E+1
	300	3.89 E 0			3.09 E+1

* E+a indicates $\times 10^{+a}$.
E−a indicates $\times 10^{-a}$.

TABLE 6—SUMMARY OF MODEL DISCRIMINATION BY CLASSICAL APPROACH

Model no.	Criteria 1	2	8
1	√	√	√
2	×	×	×
8	×	×	×
4	√	√	√
5	×	×	√
6	×	×	×
7	×	×	×
8	√	×	√
9	√	√	×
10	×	×	×
11	×	×	×
12	√	√	×
18	√	×	×
14	×	×	×
15	×	×	√
16	√	×	√
17	√	×	√
18	×	×	√
19	×	×	×
20	√	×	√
21	√	×	×
22	√	√	×
28	√	×	×
24	√	√	×

√ satisfies criterion.
× does not satisfy criterion.

A statistical method[16] was employed to choose between the rival models. In this method, the magnitude of the non-intrinsic parameter λ, given by equation (9)

$$r - 0.5[r_4 + r_1] = \lambda[r_1 - r_4] + \epsilon \qquad (9)$$

determines which of the two models represents the data adequately; if model 4 represents the data satisfactorily, then the confidence interval of λ includes −0.5 and model 1 is rejected, and *vice versa*, if the confidence interval of λ includes +0.5. The results summarised in Table 7 indicate that model 4 is preferred to model 1 at all the temperatures, for the confidence interval of λ in none of these cases is anywhere near +0.5.

TABLE 7—VALUES OF NON-INTRINSIC PARAMETER, λ

Temp. °C	λ	Standard error	Confidence interval of λ
240	−0.872	0.077	−0.184 to −0.560
255	−0.694	0.230	−0.131 to −1.257
270	−0.919	0.368	−0.031 to −1.807
285	−0.851	0.161	−0.457 to −1.244
300	−0.568	0.029	−0.497 to −0.639

Graphical test for model 4: The plots of $[\bar{p}_A - \bar{r}_A]$ *vs* $[\bar{p}_A/\bar{p}_O]$ and $[\bar{p}_O/-\bar{r}_A]$ *vs* $[\bar{p}_O/\bar{p}_A]$ for model 4 are shown in Figs. 6 and 7. These plots take into account the variation in the mean values of partial pressures of alcohol and oxygen. In these figures, the solid lines indicate the least squares fit. The linearity existing in these plots shows the validity of the two-stage redox model as well as the assumptions

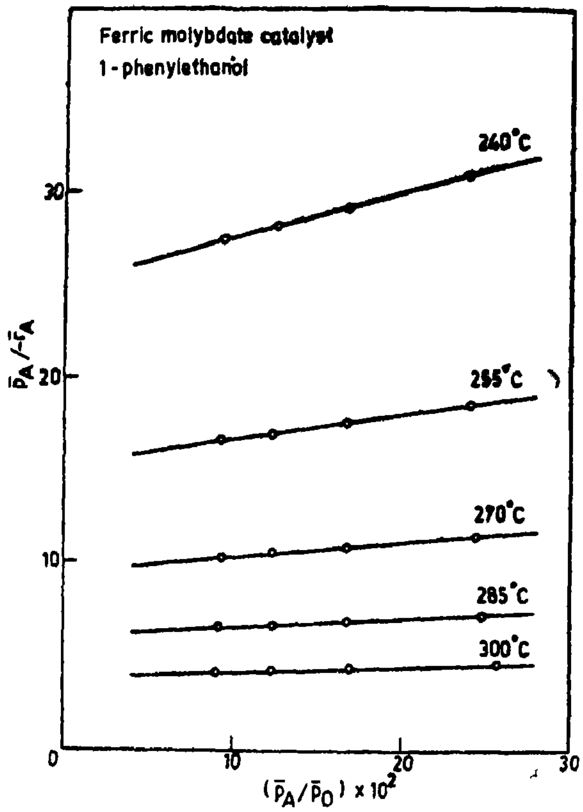


Fig. 6. Plot of $(\bar{p}_A/-\bar{r}_A)$ *vs* $(\bar{p}_A/\bar{p}_O)$.

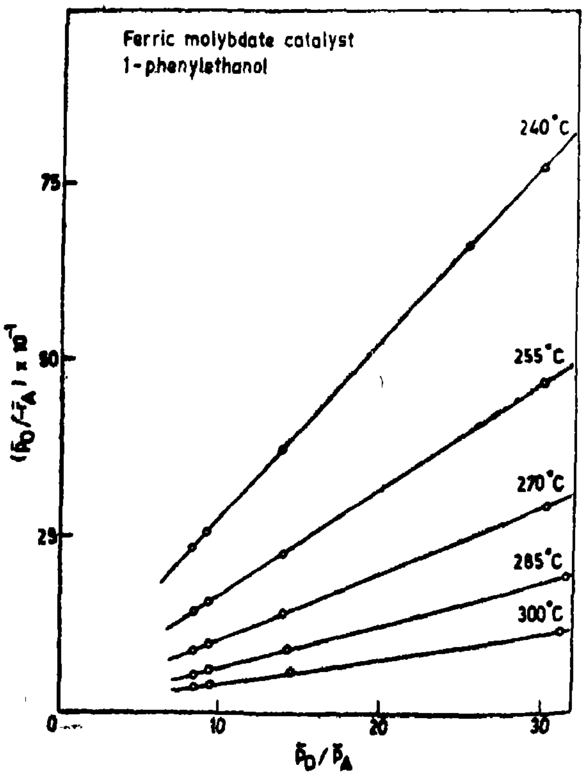


Fig. 7. Plot of $(\bar{p}_O/-\bar{r}_A)$ *vs* $(\bar{p}_O/\bar{p}_A)$.

Table 8—Rate Constants, by Least Squares Linear and Non-linear Regression

Temp. °C	$k_A \times 10^2$ mol/h(g)(atm) a	$k_A \times 10^2$ mol/h(g)(atm) b	$k_O \times 10^2$ mol/h(g)(atm)$^{0.5}$ a	$k_O \times 10^2$ mol/h(g)(atm)$^{0.5}$ b	Sum of squares of residuals a×10^{1a}	Sum of squares of residuals b×10^{1a}
240	3.97	3.98	2.06	2.05	8.80	6.81
255	6.80	6.61	3.78	3.48	20.10	4.50
270	10.68	10.60	5.85	5.93	12.15	4.74
285	16.92	16.70	9.48	9.66	17.16	7.27
300	25.88	25.40	15.91	15.90	12.80	9.90

a = linear regression, b = nonlinear regression.

made regarding the order of the reaction, *viz.* m = 1 and n = 0.5.

Non-linear least squares estimation of parameters of selected model : The integrated rate equation representing the system is

$$\frac{1}{-\bar{r}_A} = \frac{1}{k_A\bar{p}_A} + \frac{N}{k_O\bar{p}_O} \quad (10)$$

where $\bar{p}_A$ and $\bar{p}_O$ are given by equations (6) and (8). The rate constants in equation (10) were estimated using non-linear least squares method[17]. These values are incorporated in Table 8. It is seen from the Table that the use of non-linear least squares technique has resulted in a decrease of sum of squares of residuals.

The rate constants when plotted (Fig. 8) showed that they followed Arrhenius law. In the non-linear estimation of activation energy and pre-exponential factor a reparametrized temperature was used[18].

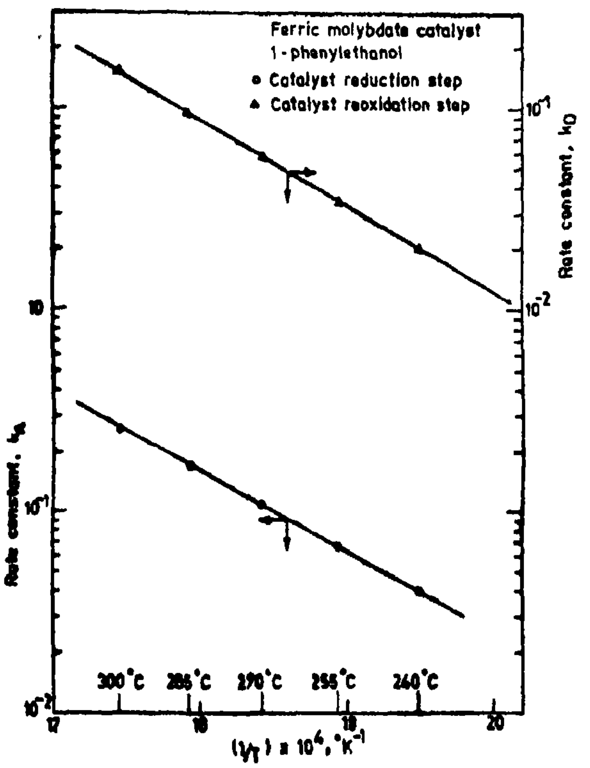


Fig. 8. Arrhenius plots.

The Arrhenius equation was modified as

$$k = A' \exp[-E/R'T'] \quad (11)$$

where

$$\frac{1}{T'} = \frac{1}{T} - \frac{1}{\bar{T}} \quad (12)$$

and

$$\frac{1}{\bar{T}} = \frac{1}{ut}\sum_{i=1}^{ut}\frac{1}{T_i} \quad (13)$$

ut in equation (13) represents the number of temperature levels. The activation energy and pre-exponential factor estimated by the non-linear method are given in Table 9.

Table 9—Activation Energies and Arrhenius Frequency Factors

Parameter	Catalyst reduction step	Catalyst reoxidation step
E_a kcal mol^{-1}	17.486	19.0
log A	20.300	20.6

Summary and conclusions : Vapour phase oxidation of 1-phenylethanol to acetophenone over ferric molybdate catalyst was studied in the temperature range 240-300° in the absence of inter- and intraphase diffusion. The reaction is adequately described by the redox equation (14).

$$-\frac{1}{r_A} = \frac{1}{k_A p_A} + \frac{0.5}{k_O p_o^{0.5}} \quad (14)$$

It was observed that the catalyst reduction and reoxidation steps proceeded at comparable rates.

Acknowledgement

Fruitful discussions with Professor D. S. Viswanath are gratefully acknowledged.

Notation

- E_a activation energy, kcal mol^{-1}
- F_A flow rate of 1-phenylethanol, mole/hr
- K_A and K_O equilibrium constants for adsorption of 1-phenylethanol and adsorption of oxygen
- k overall reaction rate constant
- k_A rate constant for catalyst reduction step, mol/(g)(h)(atm)
- k_O rate constant for catalyst reoxidation step, mol/(g)(h)(atm)$^{0.5}$
- k'_O and k_d adsorption and desorption rate constants of oxygen
- m order of reaction with respect to 1-phenylethanol

N moles of oxygen required to oxidize 1 mole of 1-phenylethanol
n order of reaction with respect to oxygen
p_A partial pressure of 1-phenylethanol, std. atm
p_O partial pressure of oxygen, std. atm
R rate number
$-r$ observed rate of reaction
$-r_A$ rate of reaction, mole of 1-phenylethanol/(g)(h)
Re Reynolds number
Sc Schmidt number
T temperature K
W weight of catalyst, g
x_A conversion, mole of 1-phenylethanol converted per mole fed
λ non-intrinsic parameter
ϵ random experimental error

Subscripts

i initial
f final

Superscript

– mean value

References

1. H. ADKINS and W. R. PETERSON, *J. Am. Chem. Soc.*, 1931, **53**, 1512.
2. N. PERNICONE, G. LIBERTI and L. ERSINI, Proc. Fourth Int. Congress Catal., Moscow, 1968, p. 287.
3. J. NOVAKOVA, P. JIRU and V. ZAVADIL, *J. Catal.*, 1971, **21**, 143.
4. P. JIRU, B. WICHTERLOVA and T. TICHY, Proc. Third Int. Congress Catal., Amsterdam, 1965, Vol. 1, p. 199.
5. N. P. EVMENENKO and YA. B. GOROKHOBATSKII, *Kinet. Catal.* (*Engl. Transl*), 1970, **11**, 104.
6. M. NIWA, M. MIZUTANI, M. TAKAHASHI and MURAKAMI, *J. Catal.*, 1981, **70**, 14.
7. G. D. KOLOVERTNOV, G. K. BORESKOV, V. A. DZISKO, B. I. POPOV, D. V. TARASOVA and D. G. BELUGINA, *Kinet. Catal.* (*Engl. Transl.*), 1965, **6**, 950.
8. G. R LAPPINS and L. C. CLARK, *Anal. Chem.*, 1951, **23**, 541.
9. V. W. REID and D. G. SOLOMON, *Analyst* (*London*), 1955, **80**, 704.
10. F. YOSHIDA, Y. RAMASWAMY and O. A. HOUGEN, *AIChE J.*, 1962, **8**, 5.
11. P. B. WEIZ and J. S. HICKS, *Chem. Eng. Sci.*, 1962, **17**, 265.
12. A. A. MASSALDI and J. A. MAYMO, *J. Catal.*, 1969, **14**, 61.
13. P. MARS and D. W. VAN KREVELEN, *Chem. Eng. Sci.*, (*Special Suppl.*), 1954, **3**, 41.
14. J. G. FIRTH and H. B. HOLLAND, *Trans. Faraday Soc.*, 1969, **65**, 189.
15. F. G. DWYER, *Catal. Rev.*, 1972, **6**, 264.
16. R. MEZAKI and J. R. KITTREL, *Can. J. Chem. Eng.*, 1966, **44**, 285.
17. P. J. REDDY and P. S. MURTI, *Indian J. Technol.*, 1971, **9**, 161.
18. T. I. PETERSON, *Chem Eng. Sci.*, 1962, **17**, 203.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1007-1009

Chemical Constituents of *Garuga pinnata* Roxb.

MEENA HARIBAL, J. B. HANUMAN, A. K. MISHRA and B. K. SABATA*

Department of Chemistry, Indian Institute of Technology, Powai, Bombay-400 076

Hydrocarbons, n-alkanols, esters, ketone, fatty acids, sterols and a new branched secondary alcohol, 6-propyltetradecan-7-ol, have been isolated from the petrol extracts of *G. pinnata* leaves and stem bark.

GARUGA pinnata Roxb. belongs to the family Burseraceae. The juice of the leaves mixed with honey is given in asthama. The juice of the stem is used as remedy for the opacity of conjuctiva. The decoction of the roots is used for pulmonary infections[1]. The aqueous extract and the ethanolic extract have been found to possess antiinflammatory and antiallergic activities[2].

Burseraceae family consists of about 20 genera having about 600 species of plants. Hardly, less than 5% of the plants have been chemically investigated. The major work done, is on the chemical examination of the gum exudates of these plants. Number of terpenes particularly di- and tri-terpenes from the genera *Canarium*[3,4], *Commiphora*[5,6] and *Boswellia*[7-9] and lignans from the genus *Bursera*[10] have been isolated. Amentoflavone, a biflavonoid, has been isolated from *G. pinnata* by Rahaman *et al*[11]. No systematic chemical investigations of these plants have been reported, hence the detailed chemical investigation of *G. pinnata* was undertaken.

The hot petrol extracts, cold acetone and methanol extracts of the leaves and stem bark have been investigated. In the present paper we report the isolation and characterisation of some of the known aliphatic compounds and a new branched secondary aliphatic alcohol from the petrol extracts of the leaves and the stem bark. All these compounds except for sitosterol, are being reported for the first time from the family *Burseraceae*.

Experimental

Petroleum ether extract of leaves : The powdered dry leaves (4 kg) were extracted successively with hot petroleum ether (b.p. 60-80°) in Soxhlet extractors. The petrol extract of the leaves (25 g) was chromatographed over silica gel, using petrol-ethyl acetate-methanol solvent system. The column was monitored by tlc, and sixteen different fractions were collected. These on further resolution by column chromatography and preparative layer chromatography yielded fractions A to F, which showed single spots on tlc. However, except for fraction D, all the remaining fractions were found to be mixtures of the homologous compounds on further detailed glc and mass spectral analysis, indicating that a single spot on tlc may not necessarily be due to a single compound, particularly so in the case of waxes.

Results and Discussion

Fraction A : Fraction A was least polar compound obtained from the column chromatography of the petroleum ether extract. It was semi-solid. The ir spectrum showed peaks for saturated hydrocarbon. Glc analysis on Dexil 300 showed it to be a mixture. The mass spectrum showed it to be a mixture of straight chain and branched chain saturated hydrocarbons. The highest peak was observed at *m/e* 240, indicating that heptadecane may be present as one of the components.

Fraction B : Fraction B on repeated crystallisation from ethyl acetate gave compound (B1) as white granules, m.p. 82-83° ; ν_{max} (nujol) 3300 (OH), 1120 and 720 cm^{-1} ; δ ($CDCl_3$) 0.86 (t, *J* 6 Hz, terminal Me), 1.25 (br, s), 3.85 (t, *J* 6 Hz CH_2O) ; *m/e* 410 (M^+), 392 ($M^+ - 18$) and successive loss of 14 mass units. On the basis of the above spectral data and by comparing it with the available literature data[12], it was identified as n-octacosanol.

The mother liquor of the above fraction on concentration deposited white granules, m.p. 83-84° ; ν_{max} (nujol) 3300 (OH), 1065 and 710 cm^{-1}. The mass spectrum showed it to be a mixture of n-alkanols. It showed weak peaks at *m/e* 522, 494, 480, 466, 452 and 438 corresponding to the M^+ peaks of C_{36}, C_{34}, C_{33}, C_{32}, C_{31} and C_{30} alkanols. The intense peaks due to loss of water ($M^+ - 18$) from the above corresponding M^+ peaks were observed at *m/e* 504, 476, 462, 448, 434 and 420.

Fraction C : Fraction C was recrystallised from ethyl acetate, m.p. 85-86° ; ν_{max} (nujol) 1735 (ester C=O), 1180 and 720 cm^{-1} ; δ ($CDCl_3$) 0.80 (t, not well defined), 1.22 (br, s), 2.25 (t, *J* 6 Hz, ($CO-CH_2$) and 4.08 (t, *J* 6.5 Hz, CH_2-O-CO). The EI–MS spectrum was characteristic of the mixture of long chain esters. It showed M^+ peaks at *m/e* 928, 900, 862, 844, 816, 788, 760 and 732 corresponding to the esters of the chain lengths C_{62}, C_{60}, C_{58}, C_{56}, C_{54}, C_{52} and C_{50} carbon atoms. The mass spectrum also showed two more groups of intense peaks. The major peaks at *m/e* 569, 481, 453, 425, 397, 369, 341, 373, 285 and 257

were due to acid moieties ($R-COO^{+}H_2$) of esters which correspond to the acids having C_{34} to C_{16} even number of carbon atoms. The other intense group of peaks were observed at *m/e* 476, 448, 420, 392 and 364, were due to the C_{34}, C_{32}, C_{30}, C_{28} and C_{26} alcohols, which may be due to the β-cleavage of the esters.

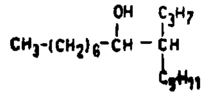
Fraction D: Fraction D was obtained by preparative layer chromatography, m.p. 81-82°; ν_{max} (nujol) 1705 (ketone) and 720 cm^{-1}; δ ($CDCl_3$) 0.84 (t, *J* 5 Hz), 1.28 (br, s), 2.31 (t, *J* 7.5 Hz); EI−MS : *m/e* 422 (M^+), 407 (M^+-15), 225 (peak), 240 (M^+, $C_{16}H_{32}$) and 197. On the basis of the above spectral data and by comparison with the literature data[13], it was identified as 15-nonacosanone.

Fraction E: Fraction E was crystallised as white flakes from methanol, m.p. 76-78°; ν_{max} (nujol) 3500-2900 (OH), 1700 (acid C=O), 1360, a number of bands 1350-1180 (*trans*−$(CH_2)_n$−chain), 930 and 715 cm^{-1}. δ ($CDCl_3$) 0.86 (t, *J* 5.5 Hz), 1.25 (br, s), 2.35 (t, *J* 5H, CH_2-CO). The ir spectrum was similar to that of the authentic sample of palmitic acid. The above spectral data indicate it to be a fatty acid. The methyl ester of the acid was prepared in the usual method by the addition of CH_2N_2. The product obtained (semi-solid) was purified by passing through a small silica gel filtration column, ν_{max} (nujol) 1735 (ester C=O), 1180, 1105 and 710 cm^{-1}; EI−MS : *m/e* 298, 270, 242, 185, 157, 143, 129, 115, 111, 101, 97, 88 and 74. The glc analysis of the methyl ester was carried out on SE−30 (10%) at 245° and the retention times were compared with those of the authentic samples. On the basis of the glc analysis it was found to be a mixture of capric acid (11.8%), myristic acid (4.19%), palmitic acid (54.8%) and stearic acid (18.22%) along with the small amount of unsaturated acids (11.3%).

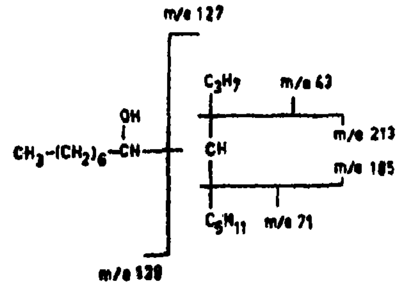
Fraction F: Fraction F was recrystallised from methanol as fine needles giving positive Liebermann-Buchard test for steroids, m.p. 133-34°; ν_{max} (nujol) 3450 (OH), 1630 (unsaturation), 1250, 1050, 950 and 925 cm^{-1}; δ ($CDCl_3$) 0.67 (t, 3H), 0.80 (d, 3H), 0.82 (t, 3H), 0.92 (d, 3H), 1.59 (br, s, D_2O-exchangeable), 3.50 (m, 1H), 5.06 (t, 1H) and 5.36 (br, d, 2H); EI−MS : *m/e* 414, 412, 400, 273, 255, 231, 299, 213, 399, 381, 329, 303, 392, 379, 327, 301, 385, 367, 315 and 219. On the basis of the above spectral data it was found to be a mixture of phytosterols. The mass spectral fragmentations showed the presence of sitosterol, stigmasterol and campesterol[14] of which sitosterol was a major component.

Petroleum ether extract of stem bark: The stem bark was also subjected to the similar treatment as it was done for the leaves. Hydrocarbon mixture, sitosterol and fatty acid mixture containing myristic acid (23%), palmitic acid (46%) and stearic acid (28%) as major acids were isolated and characterised on the basis of spectral and chemical studies. Besides these a new branched secondary alcohol, compound (G) was isolated and characterised on the basis of the spectral data.

Characterisation of compound G: Compound G was purified by preparative layer chromatography as white crystalline compound, m.p. 74-76°; ν_{max} (nujol) 3300-3500 (OH), 1250, 1100 and 720 cm^{-1}; δ ($CDCl_3$) 0.88 (t, 9H), 1.25 (br, s, 26H), 3.85 (m, 1H); EI−MS : *m/e* 256, 213, 185, 171, 157 and 129 (base peak). The above spectral data indicated it to be a saturated secondary alcohol. The mass spectrum showed M^+ peak at 256 indicating it to have a probable molecular formula $C_{17}H_{36}O$. The peak at *m/e* 213 (M−43) indicated the presence of C_3H_7 unit. The intense peak at *m/e* 129 ($C_8H_{17}O$) might be due to α-splitting of a secondary alcohol in which hydroxy group is retained. The fragmentation pattern below *m/e* 129 was similar to that of a straight chain compound, *i.e.* successive loss of 14 mass units, indicating that this fragment was a straight chain fragment. On the basis of mass spectral and pmr spectral data a tentative structure I has been assigned to this alcohol and Scheme 1 shows the formation of the important fragment ions.



I



Scheme 1

References

1. R. N. Chopra, S. L. Nayar and I. C. Chopra, Glossary of Indian Medicinal Plants, C.S.I.R., New Delhi, 1956.
2. S. R. Amladi, Personal communication.
3. C. W. M. Bandaranayke, *Phytochemistry*, 1980, **19**, 255.
4. V. K. Hinge, S. K. Paknikar, K. G. Das, A. K. Bose and S. C. Bhattacharyya, *Tetrahedron*, 1966, **22**, 2861.
5. Maradudu, *Phytochemistry*, 1982, **21**, 677.
6. V. D. Patil, U. R. Nayak and Sukh Dev, *Tetrahedron*, 1973, **29**, 341.
7. R. Nicoletti, C. Santarelli and N. L. Forcellese, *Tetrahedron Lett.*, 1966, 3783.

8. G. P. COTTRELL and T. G. HALSALL, *J. Chem. Soc.*, 1968, 2762.

9. R. PARDHY and S. C. BHATTACHARYYA, *Indian J. Chem.*, *Sect. B*, 1978, **16**, 170.

10. C. B. S. RAO, "Chemistry of Lignans", Andhra University Press, Waltair, 1978, p. 89, and references therein.

11. F. Q. ANSARI, W. H. ANSARI and W. RAHAMAN, *Indian J. Chem.*, *Sect. B*, 1978, **16**, 846.

12. A. POLLARD, A. C. CHINBAL and S. H. PIPER, *Biochem. J.*, 1933, **27**, 1869.

13. SMEDLEY and COLLISON, *Biochem. J.*, 1931, **25**, 609.

14. S. S. FRIEDLAND, G. H. LANE, R. T. LOGMAN, K. E. TRAIN and M. J. O'NEALM, *Anal. Chem.*, 1959, 31. 169.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1010-1012

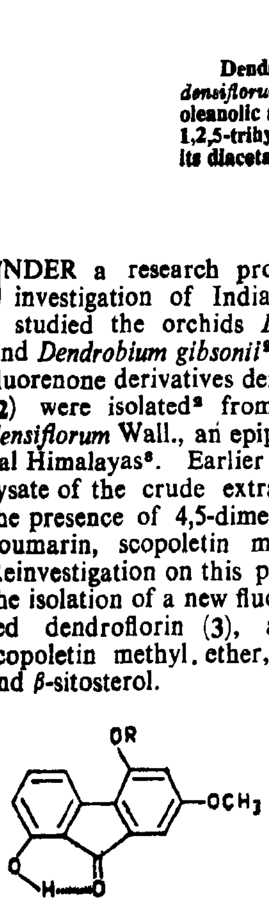
On the Chemistry of Indian Orchidaceae Plants. Part-III†. Dendroflorin, a New Fluorenone Derivative from *Dendrobium densiflorum* Wall.

SUNIL K. TALAPATRA*, SRABANI BOSE, ASOK K. MALLIK‡ and BANI TALAPATRA*

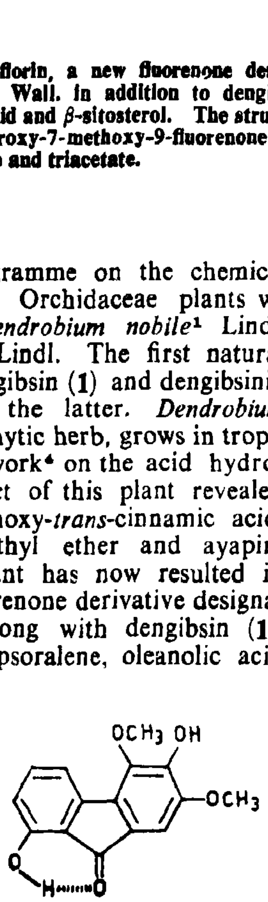
Department of Chemistry, University College of Science, Calcutta-700 009

Dendroflorin, a new fluorenone derivative has been isolated from *Dendrobium densiflorum* Wall. In addition to dengibsin (1), scopoletin methyl ether, psoralene, oleanolic acid and β-sitosterol. The structure of dendroflorin has been established as 1,2,5-trihydroxy-7-methoxy-9-fluorenone (3) from the spectral properties of itself and its diacetate and triacetate.

UNDER a research programme on the chemical investigation of Indian Orchidaceae plants we studied the orchids *Dendrobium nobile*[1] Lindl. and *Dendrobium gibsonii*[2] Lindl. The first natural fluorenone derivatives dengibsin (1) and dengibsinin (2) were isolated[2] from the latter. *Dendrobium densiflorum* Wall., an epiphytic herb, grows in tropical Himalayas[3]. Earlier work[4] on the acid hydrolysate of the crude extract of this plant revealed the presence of 4,5-dimethoxy-*trans*-cinnamic acid, coumarin, scopoletin methyl ether and ayapin. Reinvestigation on this plant has now resulted in the isolation of a new fluorenone derivative designated dendroflorin (3), along with dengibsin (1), scopoletin methyl. ether, psoralene, oleanolic acid and β-sitosterol.



1 : R=H
6 : R=COCH$_3$

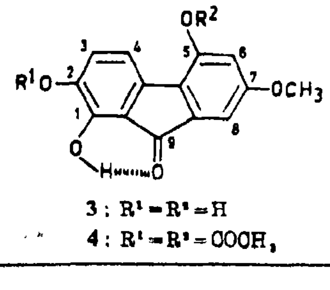


2

Dendroflorin (3), m.p. 230°, $C_{14}H_{10}O_5$ (M^+258), $[\alpha]_D \pm 0°$, isolated as red needles from the chloroform extract of the whole orchid, gave positive $FeCl_3$ colouration and exhibited ir bands [3380(OH) and 1695 cm^{-1} (conjugated C=O)] close to those of 1 and 2. It formed a diacetate (4) (through acetylation of both free phenolic OH groups under mild conditions) and a triacetate (5). The uv and visible spectral data of 3, 4 and 5 (Table 1) resembled closely those of 1, its monoacetate (6) and its diacetate (7)[2] respectively indicating the presence of a fluorenone chromophore with similar oxygenation pattern. The structure of dendroflorin was established from comparative studies on the chemical shifts of its aromatic protons with those of 4 and 5.

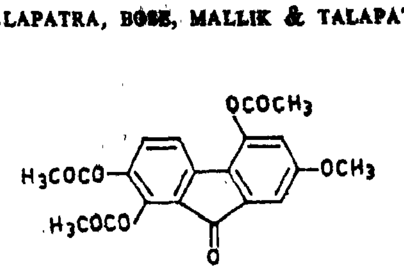
TABLE 1—UV AND VISIBLE SPECTRAL DATA OF DENDROFLORIN (3), DENGIBSIN (1) AND THEIR ACETATE DERIVATIVES

Compound	λ_{max} (EtOH) nm (log ε)	λ_{max} (EtOH) nm (log ε)
Dendroflorin (3)	259(4.60), 279(4.81), 383.5(4.31) and 485.5 (3.36)	272(4.65) and 520(3.54)
Dengibsin (1)	267(5.86), 275(5.40), 338(4.34) and 479.5(4.08)	291.5(5.45) and 549.5(4.08)
Dendroflorin diacetate (4)	244(4.16), 257(4.15), 272(4.09) and 447(3.20)	——
Dengibsin monoacetate (6)	243(4.29), 260(4.44), 271(4.42), 334(3.64) and 446.5(3.31)	——
Dendroflorin triacetate (5)	258(4.32), 267(4.30), 327.5(3.21) and 424.5(3.26)	——
Dengibsin diacetate (7)	258(4.46), 267(4.47) and 426(2.96)	——



3 : R[1] = R[2] = H
4 : R[1] = R[2] = COCH$_3$

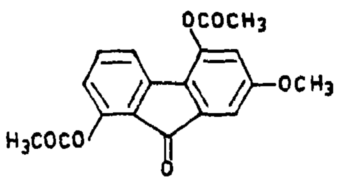
† For Parts I and II see Refs. 1 and 2.
‡ Department of Chemistry, Jadavpur University, Calcutta-700 032.



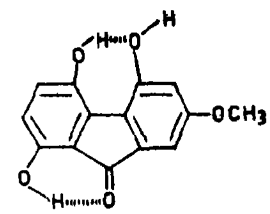
5

The ^{1}H nmr spectrum of dendroflorin exhibited signals for one aromatic OCH_3 (δ 4.14, 3H, s), one chelated phenolic OH (δ 8.48, 1H, s, exchangeable with D_2O) and four aromatic protons [δ 6.61 (1H, d, *J* 9 Hz), 6.92 (1H, d, *J* 9 Hz) and 6.83 (2H, br s)]; no signal for any of the two free phenolic OH groups was discernible. The two-proton broad singlet at δ 6.83 was due to two *meta*-disposed aromatic protons as evident from the ^{1}H nmr spectra of **4** and **5** in each of which signals for two *meta*-coupled protons and two *ortho*-coupled protons appeared (Table 2) in conformity with their structures. Dendroflorin is, therefore, a monomethoxy-trihydroxyfluorenone in which one benzene ring bears the *ortho*-disposed protons and the other the *meta*-disposed protons. In dendroflorin diacetate (**4**) one *ortho*-coupled proton and one *meta*-coupled proton were found to suffer downfield shifts of 0.46 and 0.26 ppm respectively compared to those of dendroflorin (**3**). Thus, the two free phenolic OH groups are present in two different rings. Since only one *meta*-coupled proton was deshielded on acetylation of the free phenolic OH groups, there should be no OH *meta* to the chelated OH. Hence, the ring bearing the chelated OH contains the *ortho*-disposed protons, *i.e.* the OH groups in this ring would be either 1, 2 or 1, 4. The other ring, which definitely contains the *meta*-disposed protons, could accommodate the free OH only at the 5-position in accordance with the aforesaid arguments. Thus, the structure of dendroflorin should be either **3** or **8**. The structure **3** was finally settled from the fact that acetylation of the chelated phenolic OH (by converting **4** to **5**) did not cause appreciable deshielding of any aromatic proton (Table 2).

Furthermore, the lower field aromatic proton in the ^{1}H nmr spectrum of dendroflorin triacetate (**5**), which is an acetoxy derivative of dengibsin diacetate (**7**), appeared at δ 7.13 (d, *J* 8 Hz). In case of **7**, H-2 appeared at δ 7.57 (dd, *J* 7.5 and 1.5 Hz)[a], the presence of a *meta*-acetoxy group (*i.e.* at C-4) should not be expected to shield it by ~0.45 ppm thus excluding the possibility of structure **8** for dendroflorin. Moreover, structure **8** and also the 1,2,8-trihydroxy-6-methoxy-9-fluorenone structure for dendroflorin contain two chelated OH groups and hence are untenable.



7



8

Psoralene was identified from its ir and ^{1}H nmr spectral data[8] and the other isolates were characterised by direct comparison (m.m.p., co-tlc and ir) with their authentic samples previously isolated in our laboratory[6,7].

Experimental

Melting points were determined in open capillaries in an electrical metal bath and are uncorrected. The uv spectra were measured in aldehyde-free ethanol with a Varian 634 S spectrophotometer. The ir spectra were run in KBr pellets or $CHCl_3$ on either a Pye-Unicam SP 1025 or a Perkin-Elmer 782 spectrophotometer. The ^{1}H nmr spectra were recorded in $CDCl_3$ or d_6-acetone on Varian CFT-20 (80 MHz) or JEOL FX-100 (100 MHz) or Varian XL-200 (200 MHz) spectrometer. The mass spectrum of **3** was run on 70 ev using a direct insertion probe. The silica gel used for column chromatography was of 100-200 mesh, unless otherwise stated, and the tlc experiments were done on silica gel G. Petrol refers to light petroleum, b.p. 60-80°.

Extraction : Air-dried and powdered whole plant *D. densiflorum* (1 kg), collected from Darjeeling District, was extracted in Soxhlet apparatus with

TABLE 2—^{1}H NMR SPECTRAL DATA OF DENDROFLORIN (3), ITS DIACETATE (4) AND TRIACETATE (5)[a]

Compd. no.	Chemical shifts (δ), multiplicities and coupling constants (Hz)							
	$C_1-OH/OCOCH_3$[b]	$C_2-OH/OCOCH_3$[b]	H-3	H-4	$C_5-OH/OCOCH_3$[b]	H-6	C_7-OCH_3	H-8
3	8.48[c]	—	6.61, d (9)	6.92, d (9)	—	6.83, bs	4.14	6.83, bs
4	9.01[c]	2.38	7.07, d (8)	6.83, d (8)	2.44	7.09, d (2)	4.12	6.87, d (2)
5	2.24	2.28	7.13, d (8)	6.91, d (8)	2.32	7.05, d (2)	3.84	[illegible], d (2)

[a] For 3, 80 MHz, d_6-acetone ; for 4, 200 MHz, $CDCl_3$ and for 5, 100 MHz, $CDCl_3$.
[b] The assignment of the $OCOCH_3$ signals of 4 and 5 may be interchanged.
[c] Disappeared on deuteration.

petrol and chloroform in succession for 40 h each. The concentrates of the extracts were chromatographed separately over silica gel (60-100 mesh) using solvents and solvent mixtures of increasing polarity as eluents.

Compounds from petrol extract :

β-Sitosterol : The early petrol-ethyl acetate (9 : 1) eluates afforded β-sitosterol (0.005%), m.p. and m.m.p. with an authentic sample 137° ; $[\alpha]_D - 37°$ ($CHCl_3$).

Psoralene : The later petrol-ethyl acetate (9 : 1) eluates on rechromatography over silica gel furnished psoralene (0.001%), crystallising from chloroform-petrol in colourless needles, m.p. 160°.

Scopoletin methyl ether : The concentrate of the petrol-ethyl acetate (4 : 1) eluates on rechromatography over silica gel afforded scopoletin methyl ether (0.003%), crystallising from chloroform-petrol in colourless needles, m.p. and m.m.p. with an authentic sample 143°.

Oleanolic acid : The concentrate of the petrol-ethyl acetate (7 : 3) eluates on repeated chromatography over silica gel furnished oleanolic acid (0.001%), m.p. and m.m.p. with an authentic sample 304° ; acetate, m.p. 260°, $[\alpha]_D + 71.4°$ ($CHCl_3$).

Compounds from the chloroform extract :

Dengibsin (**1**) *:* The concentrate of the early petrol-ethyl acetate (7 : 3) eluates on rechromatography over silica gel furnished dengibsin (**1**) (0.001%), crystallising from acetone-petrol in deep red needles, m.p. and m.m.p. with an authentic sample 227°.

Dendroflorin (**3**) *:* The concentrate of the later petrol-ethyl acetate (7 : 3) eluates on repeated chromatography over silica gel afforded dendroflorin (**3**) (0.0004%), crystallising from acetone-petrol in red needles, m.p. 230° ; green colouration with $FeCl_3$ solution ; ν_{max} (KBr) 3380, 1695, 1630, 1520 and 1295 cm^{-1} ; m/z 258 (M^+, 92.2%), 243 (100), 215 (22), 187 (8.3), 137 (8.0) and 129 (7.9).

Dendroflorin diacetate (**4**) *:* To a solution of dendroflorin (**3**) (2 mg) in pyridine (0.5 ml) 2 drops of a solution of Ac_2O in pyridine (prepared by adding 2 drops of Ac_2O to 1 ml pyridine) was added at 0° and the mixture was kept in the deep freeze for 17 h. Usual work up of the reaction mixture furnished dendroflorin diacetate (**4**), crystallising from chloroform-petrol in orange needles (2 mg), m.p. 168° ; ν_{max} ($CHCl_3$) 3320, 1768, 1712, 1605, 1520, 1425, 1225, 1205, 1015 and 930 cm^{-1}.

Dendroflorin triacetate (**5**) *:* Dendroflorin diacetate (**4**) (2 mg) was acetylated (Ac_2O/Py, 24 h) at room temperature and the product was crystallised from chloroform-petrol to afford dendroflorin triacetate (**5**) as yellow needles (1.5 mg), m.p. 172° ; ν_{max} (KBr) 1760, 1712, 1610, 1485, 1368, 1305, 1195, 1185, 1020 and 900 cm^{-1}.

Acknowledgement

The authors are thankful to Mr. D. F. Dance (Stirling University, U. K.) for mass spectral measurements, and to Professor U. R. Ghatak (I.A.C.S., Calcutta) and Dr. A. K. Chakraborty (I.I.C.B., Calcutta) for ^1H nmr spectra. Financial assistance from U.G.C., New Delhi by way of a Senior Research Fellowship to one of the authors (S.B.) is gratefully acknowledged.

References

1. B. TALAPATRA, P. MUKHOPADHYAY, P. CHAUDHURY and S. K. TALAPATRA, *Indian J. Chem., Sect. B*, 1982, **21**, 386.
2. S. K. TALAPATRA, S. BOSE, A. K. MALLIK and B. TALAPATRA, *Tetrahedron*, 1985, **41**, in the press.
3. J. D. HOOKER, "The Flora of British India", L. Reeve and Co., London, 1890, Vol. V, p. 748.
4. J. DAHMEN, K. LEANDER, J. ROSENBLOM, *Acta Chem. Scand. Ser. B*, 1975, **29**, 627.
5. W. STECK and M. MAZUREK, *Lloydia*, 1972, **35**, 428.
6. B. TALAPATRA, A. K. MALLIK and S. K. TALAPATRA, *J. Indian Chem. Soc.*, 1981, **58**, 815.
7. B. TALAPATRA, A. BASAK and S. K. TALAPATRA, *Indian J. Chem., Sect. B*, 1983, **22**, 465.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1013

Synthesis of 2-Methyl-2-(*m*-methoxyphenyl)-cyclohexanone

SHIBA NARAYAN MAHAPATRA

Regional Research Laboratory, Bhubaneswar-751 018

Synthesis of 2-methyl-2-(*m*-methoxyphenyl)-cyclohexanone, an important intermediate towards the synthesis of resin acids has been described.

DITERPENOIDS have been known for over a century and their chemistry has come under extensive study during the past fifty years. But syntheses of these compounds have been mainly confined to the last three decades. Much of the interest in their syntheses stems from their resemblance, especially in the A and B rings, provides for a comparison of the methods used in the synthesis of the two systems.

2-Methyl-2-(*m*-methoxyphenyl)-cyclohexanone serves as an important intermediate towards resin acid syntheses. It is prepared by Grignard reaction between *m*-bromoanisole and cyclohexanone to yield 1-(*m*-methoxyphenyl)-cyclohexanol, which on dehydration using oxalic acid in toluene yielded 1-(*m*-methoxyphenyl)-cyclohexene. The cyclohexene was converted into the corresponding nitrosochloride following Ginsberg's method[1]. This was later treated with pyridine, followed by dilution with ether and extracted with Claisen alkali. The alkaline solution on acidification yielded 2-(*m*-methoxyphenyl)-cyclohex-2-enone oxime. The unsaturated ketone was regenerated from the oxime and was reduced catalytically to give 2-(*m*-methoxyphenyl)-cyclohexanone. This was subsequently methylated using methyl iodide in the presence of sodamide to yield 2-methyl-2-(*m*-methoxyphenyl)-cyclohexanone. Thus A and C rings of the resin acid are synthesised.

References

1. D. GINSBERG and R. PAPPO, *J. Chem. Soc.*, 1951, 516.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1014-1015

Synthesis of 1-Acetyl/Pentafluorophenyl-3-fluorinatedaryl-5-phenyl/furfuryl-4*H*-4,5-pyrazolines as Antifertility Agents

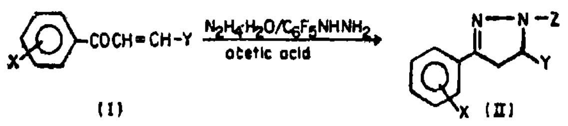
KRISHNA C. JOSHI*, V. N. PATHAK and SHARDA SHARMA

Department of Chemistry, University of Rajasthan, Jaipur-302 004

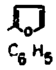
Various substituted fluorochalcones were prepared from appropriate ketones and aldehydes and two new chalcones are reported. On condensation with hydrazine hydrate or pentafluorophenylhydrazine in acetic acid, the chalcones gave the title compounds, 1-acetyl/pentafluorophenyl-3-fluorinatedaryl-5-phenyl/furfuryl-4*H*-4,5-pyrazolines (IIa-i). The compounds were screened for antiimplantation activity in adult female rats at 10 mg/kg.

THE pyrazole nucleus is reported to possess contraceptive and abortifacient activities[1-3]. Pyrazoline derivatives were synthesised and screened as antifertility agent by Sangwan and Rastogi[4] but none of these compounds could prevent pregnancy at a dose of 10 mg/kg. Keeping in view the observations that the introduction of fluorine leads to altered biological activity in many systems, we thought it worthwhile to incorporate fluorine into pyrazoline system and study whether this would lead to better antiimplantation activity in the title compounds.

The substituted fluorinated chalcones were prepared by the base catalysed condensation of fluorinated ketones and aldehydes. Two of the chalcones, 1-(3,4-difluorophenyl)-3-phenyl-2-propen-1-one and 1-(3,4-difluorophenyl)-3-(2'-furyl)-2-propen-1-one derived from 3,4-difluoroacetophenone, are being reported for the first time. On condensation with hydrazine hydrate or pentafluorophenylhydrazine in acetic acid, the chalcones gave the title compounds (IIa-i).



(I) (II)

	X	Y		Z
a	4-F	C_6H_5	a	$COCH_3$
b	2,3,4,5,6-PentaF	C_6H_5	b	$COCH_3$
c	3,4-di F	C_6H_5	c	$COCH_3$
d	4-F, 3-Me	C_6H_5	d	$COCH_3$
e	4-F		e	$COCH_3$
f	3,4-di F		f	$COCH_3$
g	3-cl, 4-F	C_6H_5	g	$COCH_3$
h	5-F, 2-Me	C_6H_5	h	$COCH_3$
i	4-F	C_6H_5	i	C_6F_5

Representative compounds were screened for their antiimplantation activity in adult female rats.

Experimental

The compounds were characterised by melting points, elemental analysis, ir, ^1H nmr and mass spectral studies. Melting points were taken on a Toshniwal apparatus and are uncorrected. Ir spectra (KBr) were recorded on a Perkin Elmer-157 G spectrophotometer. ^1H nmr spectra ($CDCl_3$) were recorded on a Bruker HX-90 spectrometer using TMS as internal standard. Mass spectra were recorded on Kratos-30 and 50 spectrometers. Purity of the compounds was checked on silica gel G tlc plates using benzene or benzene-ethyl acetate (1 : 1).

Fluorinated chalcones : Various chalcones derived from fluorinated ketones and aldehydes (**Ia-i**) were prepared by the literature method[5-9].

1-(3,4-Difluorophenyl)-3-phenyl-2-propen-1-one : 3,4-Difluoroacetophenone (0.01 mol) was treated with benzaldehyde (0.01 mol) in minimum amount of ethanol and stirred at room temperature for 30 min. Sufficient NaOH solution (2 *N*) was added to it, to render the stirred solution alkaline and the whole reaction mixture was further stirred for about 30 min. This was then neutralised with HCl (1 *N*) and diluted with water. The precipitated chalcone was filtered and recrystallised from ethanol to yield the product (60 %), m.p. 85° (Found : C, 73.6 ; H, 4.2. $C_{15}H_{10}F_2O$ requires C, 73.7 ; H, 4.1%) ; ν_{max} (KBr) 1650 cm^{-1} (C=O highly conjugated) ; ^1H nmr ($CDCl_3$) : δ 7.2 (d, C_α-*H*), 7.9 (d, C_β-*H*) and 6.5-8.0 (complex multiplet, aromatic protons).

1-(3,4-Difluorophenyl)-3-(2'-furyl)-2-propen-1-one : This was prepared by similar procedure from 3,4-difluoroacetophenone (0.01 mol) and furfuraldehyde (0.01 mol). Yield 60.6%, m.p. 155° (Found : C, 66.5 ; H, 3.5. $C_{13}H_8F_2O_2$ requires C, 66.6 ; H, 3.4%). ν_{max} (KBr) 1650 cm^{-1} (C=O highly conjugated) ; ^1H nmr ($CDCl_3$) : δ 7.25 (d, C_α-*H*), 7.9 (d, C_β-*H*) and 6.5-8.0 (complex multiplet, aromatic protons).

*1-Acetyl-3-(4'-fluorophenyl)-5-phenyl-4*H*-4,5-pyrazoline :* A mixture of 4-fluorochalcone (0.01 mol), hydrazine hydrate (0.012 mol) and glacial acetic acid

TABLE 1—ANALYTICAL DATA OF SUBSTITUTED PYRAZOLINES

Compd. no.	X	Y	Z	M.p. °C	Yield %	Molecular formula	N% Found/(Calcd.)
IIa	4-F	C_6H_5	$COCH_3$	140	86.6	$C_{17}H_{15}FN_2O$	10.1 (9.9)
IIb	2,3,4,5,6-PentaF	C_6H_5	$COCH_3$	80	80.0	$C_{17}H_{11}F_5N_2O$	8.1 (7.9)
IIc	2,4-diF	C_6H_5	$COCH_3$	160	75.0	$C_{17}H_{14}F_2N_2O$	9.5 (9.3)
IId	4,F,3-Me	C_6H_5	$COCH_3$	150	80.0	$C_{18}H_{17}FN_2O$	9.8 (9.5)
IIe	4-F	α-furyl	$COCH_3$	85	86.0	$C_{15}H_{13}FN_2O_2$	11.3 (11.4)
IIf	3,4-diF	α-furyl	$COCH_3$	155	80.0	$C_{15}H_{12}F_2N_2O$	10.3 (10.5)
IIg	3-Cl, 4-F	C_6H_5	$COCH_3$	120	85.0	$C_{17}H_{14}ClFN_2O$	8.7 (8.8)
IIh	5-F, 2-Me	C_6H_5	$COCH_3$	110	85.0	$C_{18}H_{17}FN_2O$	9.6 (9.8)
IIi	4-F	C_6H_5	C_6F_5	150	75.0	$C_{21}H_{12}F_6N_2$	6.8 (6.4)

(10 ml) was refluxed for 6-8 h. The mixture was cooled and poured into crushed ice. The resultant solid mass was filtered, washed with water and recrystallised from methanol to yield the product (86.6%), m.p. 140° (Found : N, 10. $C_{17}H_{15}FN_2O$ requires N, 9.9%) ; ν_{max} (KBr) 2800-2900 (CH_2), 1635-1665 (C=O, C=N), 1100-1400 cm^{-1} (=C−F) ; ^1H nmr ($CDCl_3$) : δ 2.3 (s, $COCH_3$), 3.2-3.7 (dd, CH_2), 5.6 (s, =C−H) and 6.5-8.0 (complex multiplet, aromatic protons) ; M^+ at m/z 282.

The other compounds **IIb-i** (Table 1) were prepared similarly using appropriate chalcone and hydrazine. In the mass spectra, the parent peak M^+ at m/z 354 (**IIb**), 300 (**IIc**) and 296 (**IId**) correspond to their molecular weights.

Antifertility activity : Four representative compounds (**IIa-d**) were screened for their antiimplantation activity. Testing was done on adult female rats of the Charles Foster strain weighing between 120-200 g body weight. The compounds were suspended in distilled water with the help of gum acacia and administered orally at 10 mg/kg P.C. once daily for 7 days. The rats were examined on day P.C. The results are summarised in Table 2.

TABLE 2—POST-COITAL ANTIFERTILITY EFFICACY IN ADULT FEMALE RATS

Compound no.	Dose[a] mg/kg	Total rats	Pregnant[b] rats	Implantations[b] mean ± SE, range
IIa	10	5	5	6.40 ± 1.11 (4-10)
IIb	10	5	4	8.25 ± 1.44 (4-10)
IIc	10	5	5	6.66 ± 1.21 (2-9)
IId	10	6	5	6.80 ± 0.86 (4-9)

[a] Days 1-5 Post-coitum, oral. [b] Day 10 Post-coitum.

Acknowledgement

The authors are grateful to Dr. S. K. Roy and Dr. M. M. Singh, Department of Endocrinology, Central Drug Research Institute, Lucknow for evaluation of antifertility activity and Dr. A. Shah, Institut für Orgeniache Chemie and Biochemie, der Universität Bonn, West Germany for providing the spectra. We are also thankful to Indian Council of Medical Research, New Delhi for financial assistance.

References

1. R. V. COOMBS and W. J. HOULIMAN, *Chem. Abstr.*, 1976, **85**, 78124.
2. D. A. HABECK and W. J. HOULIHAN, *Chem. Abstr.*, 1976, **85**, 160083.
3. E. W. BOUSQUET, M. D. MORAN, J. HARMON, A. L. JOHNSON and J. C. SUMMERS, *J. Org. Chem.*, 1975, **40**, 2208.
4. N. K. SANGWAN and S. N. RASTOGI, *Indian J. Chem.*, *Sect. B*, 1979, **18**, 65.
5. U. G. JOSHI and G. C. AMIN, *J. Indian Chem. Soc.*, 1961, **38**, 159.
6. N. M. SHAH and S. R. PARIKH, *J. Indian Chem. Soc.*, 1962, **36**, 776.
7. K. C. JOSHI and A. K. JAUHAR, *J. Indian Chem. Soc.*, 1962, **39**, 465.
8. K. C. JOSHI and A. K. JAUHAR, *J. Indian Chem. Soc.*, 1965, **42**, 787.
9. R. FILLER, U. O. BEAUCAIRE and H. H. KANG, *J. Org. Chem.*, 1975, **40**, 935.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1016-1022

Some Aspects of Protoberberine Alkaloids

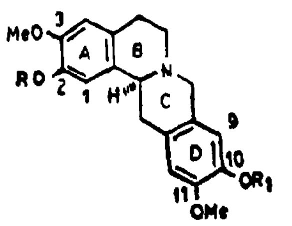
D. S. BHAKUNI

Central Drug Research Institute, Lucknow-226 001

Several protoberberine alkaloids have been isolated from *Corydalis meifolia*, *C. govaniana*, *Stephania glabra* and *Cocculus pendulus*. The structure and stereochemistry of new bases have been assigned. Biosynthesis, and positive and negative chemical ionization mass spectral studies of some protoberberine alkaloids have been carried out.

SOME twelve years ago in the Central Drug Research Institute, Lucknow we initiated a programme of research to investigate the alkaloid bearing Indian plants which either have a reputation as folk medicine or the extract of which show consistent biological activity when screened. The general pattern has been that the alkaloids from such plants are isolated. The structure and stereochemistries are determined. The pharmacological properties of the isolated compounds are studied. Finally, biosynthetic studies are carried out on compounds of biological and chemical interest. Under this programme we have investigated the alkaloids of *Corydalis govaniana*, *C. meifolia*, *Stephania glabra* and *Cocculus pendulus*. The studies carried out on the protoberberine alkaloids from these plants are reported in the present communication.

Protoberberine alkaloids of Corydalis govaniana : Reinvestigation of the leaves and stems of *C. gavaniana* (Fumariaceae), a perennial herb with bright yellow flowers that grows in the western Himalayas at an altitude of 2500-4000 meters, afforded three new tetrahydroprotoberberines[1], govadine (**1**), govanine (**2**) and corygovanine (**4**), apart from the known phthalideisoquinoline alkaloid, bicuculline. Corlumine, isocorydine, protopine and bicuculline have been isolated earlier from the roots of the plant[2]. The plant had been reported to be efficacious in many ailments[3].



1 $R=R_1=H$
2 $R=H$; $R_1=Me$
3 $R=R_1=Me$

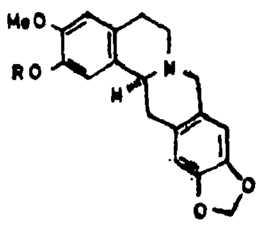
Govadine, govanine and corygovanine had in their ir spectra Bohlmann bands at 2800-2700 cm^{-1} characteristic of a tetrahydroprotoberberine nucleus[4]. This was supported by their uv spectra which had absorption maxima at 210-212 and 280-287 nm typical of tetrahydroprotoberberines[5]. Addition of alkali caused a bathochromatic shift to 230-234 and 286-294 nm, respectively in the uv spectra of these bases, thus indicating the presence of phenolic hydroxyl groups.

The nmr spectra of govadine, govanine and corygovanine revealed that these bases had a tetrasubstituted tetrahydroprotoberberine nucleus, since in each case there were only four aromatic protons. The absence of the *ortho*-coupling of the aromatic protons suggested that govadine had substituents at C-2, 3, 10 and 11 positions instead at 2, 3, 9 and 10 positions. The substituents at C-10, 11 instead of C-9, 10 in ring D was also evident by the C-8 methylene protons which appeared as a broad signal centred at δ 3.80. Govadine had only two methoxyl groups. The remaining two oxygen functions in the base were probably present as hydroxyl groups since two protons got exchanged on D_2O shake.

The pattern of the aromatic protons in the nmr spectra of govanine and corygovanine and the absence of A B quartet due to C-8 methylene protons suggested that the substituents in both these bases were also at C-10, 11 positions in ring D and not at C-9, 10 positions. Further, both bases had only one hydroxyl group since only one proton was exchanged in the nmr spectra of these bases on D_2O shake. The presence of monohydroxylic group in the bases was confirmed by acetylation. The nmr spectrum of the bases further revealed the presence of three methoxy function in govanine, whereas one methoxy and one methylenedioxy group were present in corygovanine.

Methylation of govadine with diazomethane gave *O,O*-dimethylgovadine. Under similar conditions govanine afforded *O*-methylgovanine. Both the methyl ethers were found identical in all respects including optical rotation, with (−)-norcoralydine (**3**) of known absolute configuration[6]. Thus govadine (**1**) and govanine (**2**) had the *S*-configuration at the asymmetric carbon atom. Corygovanine on treatment with diazomethane yielded *O*-methyl derivative (**5**) identical with (±)-*O*-methylcorygovanine. Govadine, govanine and corygovanine

had typical mass fragmentation of tetrahydroprotoberberines[7]. Fragmentation occurred with the cracking of ring-C through the retro-Diels-Alder process giving rise to fragments 'a' and 'b'. The fragment 'a' constituted ring-A and B while the fragment 'b' comprised mainly ring-D and the two substituent carbon atoms of ring-C. The substitution pattern in these rings further gave rise to the fragments of the corresponding mass. The ion m/z 176 arising from ion 'a' was common in the mass spectra of govadine, govanine and corygovanine and suggested the presence of one hydroxyl and one methoxy group in ring-A in each of these bases. The ion arising from fragment 'b' was at m/z 164, 150 and 148 in the mass spectra of govanine (2), govadine (1) and corygovanine (4), respectively. This suggested the presence of two methoxyl groups in 2, one methoxyl and one hydroxyl groups in 1, and one methylenedioxy group in 4.

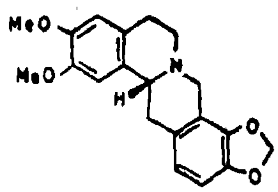


4 R=H
5 R=Me

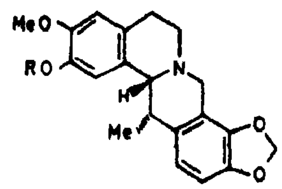
The structures 1, 2 and 4 for govadine, govanine and corygovanine, respectively were confirmed by their synthesis. Mannich condensation of (±)-*O*,*O*-dibenzyl-*N*-nororientaline using 37% formalin in the presence of glacial acetic acid gave (±)-*O*,*O*-dibenzylgovadine which on hydrogenolysis with ethanolic hydrochloric acid gave (±)-govadine. Mannich condensation of (±)-*O*-benzyl-*N*-norcodamine in the usual way furnished *O*-benzylgovanine which on treatment with ethanolic hydrochloric acid gave (±)-govanine. (+)-Corygovanine was similarly synthesized from 1-(3.4-methylenedioxybenzyl)-1,2,3,4-tetrahydro-7-benzyloxy-6-methoxyisoquinoline.

Protoberberine alkaloids of Corydalis meifolia : *Corydalis* (Papaveraceae), an ornamental genus of about 250 species of perennial herbs with underground tubers are distributed in Europe and Asia. About 25 *Corydalis* species occur in the Himalayan region and Khasi hills in India[8]. *C. meifolia* wall. is one of these species that grows at an altitude, 12000 to 15000 ft. The extracts of various *Corydalis* species are reported to be efficacious in many ailments in the Ayurvedic system of medicine[9]. Ochotensine, an alkaloid that occurs in many *Corydalis* species is reported to stimulate isolated muscles of guinea pig and of rabbit uterus, and induce a fall in blood pressure in anaesthetised cats[10]. The plant, however, appeared to have escaped the attention of chemists and pharmacologists.

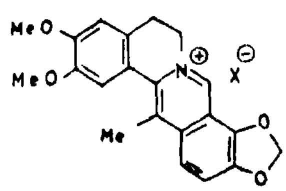
50% Alcoholic extract of *C. meifolia* when put to a broad biological screen, spasmolytic activity was confirmed in the extract[11]. In the follow up studies the activity was concentrated in the alkaloidal fraction of the alcoholic extract. Careful column and preparative thin layer chromatography of the alkaloid mixture on silica gel gave protoberberines, (+)-sinactine (6), apocavidine (8), stylopine (10), (+)-cavidine (7), cheilanthifoline (11), dehydrocavidine (9) and spirobenzylisoquinoline, yenhusomine and protopine. Of the isolated bases dehydrocavidine (9), was a new base. The remaining alkaloids though known were isolated for the first time from *C. meifolia*.



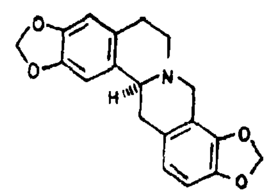
6



7 R=Me
8 R=H



9



10

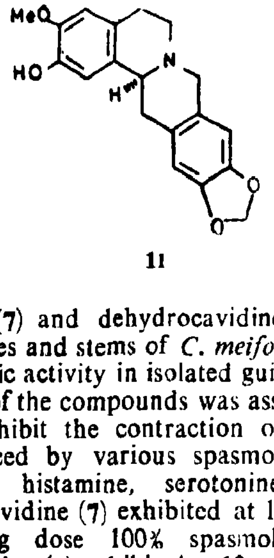
Dehydrocavidine (9) was named so because of its relationship with cavidine. In the uv spectrum of the base the absorption maxima at 347, 372 and 420 nm which remained unchanged in the presence of alkali suggested berberine type of nucleus for the base. The signals for two methoxyl groups were at δ 3.84 and 3.88, respectively and a two-proton signal at δ 6.35 was for methylenedioxy group. A three-proton singlet at δ 2.92 accounted for $C_{13}-CH_3$. The aromatic protons at C-11 and C-12 appeared together as a broad singlet at δ 7.74, one-proton singlets at δ 6.9 and 7.12 were due to aromatic C-1 and C-4 protons, respectively. The C_8-H appeared as singlet at δ 10.4. In the mass spectrum of the base the molecular ion (M^+) was at m/z 350. The other significant ions in the spectrum were at m/z 191, 177 and 145. Sodium borohydride reduction of the base gave a compound identical in all respect with (+)-cavidine (7) except optical rotation.

The alkaloid eluted with benzene from silica gel column was characterized as (+)-cavidine (7) which has been isolated from the tubers of *C. ambigua*[12]. (±)-Cavadine, named as base-II is also a natural product and had been isolated from *C. ledebouriana*[13] and *C. thalictrifolia*[14]. The conformation of 13-methyltetrahydroprotoberberines has been discussed by Jeffs[15] and it has been concluded that in compounds in which C-13 and C-13a protons are *cis*- to one another, the quinolizine system assumed a *trans*-conformation and C-13 methyl adopts an axial orientation. The compounds of this stereochemistry exhibit Bohlmann's band

in their infra-red spectrum[4]. In the ir spectrum of (+)-cavidine (7) Bohlmann's bands were at 2800-2700 cm^{-1}, confirming thus *trans*-quinolizidine conformation of B/C ring junction. The alkaloid obtained by elution of silica gel column with benzene : ethylacetate (99 : 1) was characterised as apocavidine (8). The base had earlier been isolated from *C. tuberosa*[14]. Stereochemistry of apocavidine (8) has been established by converting it into (+)-cavidine (7) of known stereochemistry[15].

Elution of silica gel column with benzene : ethyl acetate (75 : 25) afforded a base, characterised as (+)-sinactine (6). (±)- and (−)-sinactine had been isolated from *Sinomenium acutum*[16], *Fumaria species*[17], *Papaver rhoeas*[18] and *Corydalis ambigua*[19]. (+)-Sinactine (6), is however, isolated by us for the first time from *C. meifolia*. (+)-Sinactine (6) is a member of tetrahydroprotoberberine group of alkaloids. The members of this group which show levorotation have been assigned 'S' configuration at the asymmetric centre[8]. (+)-Sinactine (6) exhibits dextrorotation, hence the base must have 'R' configuration at C-13a.

Chromatography of the alkaloidal mixture-H on silica gel column afforded stylopine (10) which was isolated first from *C. tuberosa*[20]. The base subsequently has been isolated from several *Corydalis* species[21]. A phenolic tetrahydroprotoberberine alkaloid obtained from the polar chromatographic fractions is identified as cheilanthifoline (11). It was first isolated from *C. scouleri*[22]. The base subsequently has been isolated from several *Corydalis* species[21].



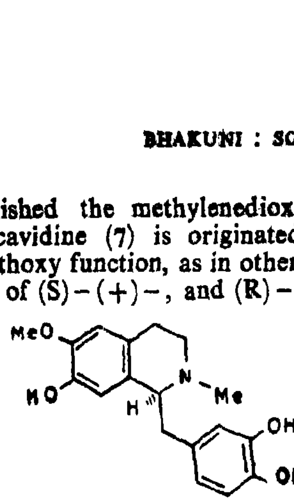
11

Cavidine (7) and dehydrocavidine (9) isolated from the leaves and stems of *C. meifolia* were tested for spasmolytic activity in isolated guinea pig ileum. The activity of the compounds was assessed by their ability to inhibit the contraction of the smooth muscles induced by various spasmogens, such as acetylcholine, histamine, serotonine and barium chloride. Cavidine (7) exhibited at 10 μg dose 80% and at 50 μg dose 100% spasmolytic activity. Dehydrocavidine (9) exhibited at 10 μg dose 20% and at 50 μg dose 40% spasmolytic activity. The bases nonspecifically blocked the effect of the above mentioned spasmogens in a dose dependent manner. The IC_{50} (concentration causing 50% inhibition) against spasmogen was found to be between 0.5 to 1.0 μg ml^{-1}. As is evident from the results the bases failed to block any of the spasmogens specifically and thus had a nonspecific spasmolytic effect.

Biogenetically the protoberberine alkaloids of *C. meifolia* could be derived in nature from suitably substituted 1-benzyltetrahydroisoquinoline precursors. Tracer experiments have shown that tetrahydroprotoberberines, scoulerine[23], isocorypalmine[24] and canadine[24] are converted into the phthalideisoquinoline narcotine. It has been proved firmly that 13-methyltetrahydroprotoberberines such as corydaline are structural variant of 1-benzyltetrahydroisoquinoline skeleton[25].

We have studied the biosynthesis of (+)-cavidine (7). The results of traces experiments are as follows. Initial feeding of (L)-[U−^{14}C] tyrosine to young plants demonstrated that the plants were actively biosynthesing cavidine (7). Subsequent feedings of tyrosine in parallel with labelled (±)-nor-reticuline, reticuline demonstrated that both were efficientl precursors of 7. Feeding of labelled (+)-protosinomenine, nororientaline and norlaudanidine showed that none of these were efficiently metabolized by the plant to form 7. The resiospecificity of ^{14}C label in the biosynthetic cavidine (7) derived from the feeding of (±)-[N−$^{14}CH_3$] reticuline was established as follows. Labelled cavidine (7) was dehydrogenated with iodine to afford dehydrocavidine (9) with essentially the same molar activity as the parent base. 9 was then treated with phenylmagnesium bromide to give 8-phenyldihydrocavidine with essentially no loss of activity. Kuhn-Roth oxidation of the compound in the usual way furnished radioactive benzoic acid (96% activity of original). Feeding of (±)-[1−^{3}H, 3−^{14}C] nor-reticuline gave labelled cavidine (7). The ^{14}C : ^{3}H ratio in the precursor was 1 : 9 whereas in biosynthetic 7, 1 : 8. The result thus established that the H atom at the asymmetric centre C-13a in cavidine remains untouched during biotransformation of the norreticuline into cavidine. The regiospecificity of the label in the biosynthetic cavidine (7) derived from (±)-[1−^{3}H, 3−^{14}C] norreticuline was demonstrated as follows. Labelled cavidine (7) was converted into its methiodide and then into its methohydroxide form with essentially no loss of radioactivity. Hofmann degradation of the methohydroxide yielded the methine-I which has essentially the same radioactivity as that of the parent base. The radioactive methine-I was treated with methyl iodide to afford methine methiodide which was passed through amberlite IR-410 anion exchange resin to give the corresponding methohydroxide, with essentially the same molar radioactivity as the parent base. Treatment of the methohydroxide with Raney Ni gave the methine-II which was then subjected to second Hofmann degradation in the usual way to give the radioactive methine-III with essentially no loss of radioactivity. Ozonolysis of methine-III furnished the radioactive formaldehyde (dimedone derivative, 90% activity of the original). Feeding of (±)-[1−^{3}H, 4′−O−$^{14}CH_3$] nor-reticuline gave labelled cavidine (7) which was heated with hydrochloric acid. The liberated radioactive formaldehyde was trapped as formaldehyde-dimethone (98% of the original activity). The results

thus established the methylenedioxy function in ring-D in cavidine (7) is originated from *ortho*-hydroxy-methoxy function, as in other cases. Parallel feedings of (S)−(+)−, and (R)−(−)−, reticu-

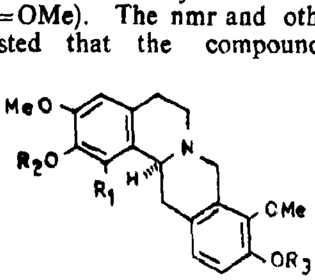


12

lines demonstrated that (R)−(−)− enantiomer was incorporated more efficiently than that of the (S)−(+)−enantiomer. The foregoing tracer experiments thus firmly established that (+)−cavidine (7) is stereospecifically biosynthesised in the plants from (R)−reticuline (12).

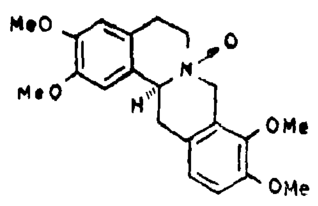
Protoberberine alkaloids of Stephania glabra : Extracts of the rhizomes of *S. glabra*, a glabrous dextrous climber indigenous to the lower Himalayas (5000-6000 ft) have long been used by the natives as an antidysenteric, antipyretic and antiasthmatic[26]. To date 17 alkaloids have been isolated from the rhizome of the plant. Some of the isolated bases possessed hypotensive and antimicrobial properties. The ethanolic extract of the rhizomes of *S. glabra*, when put to a broad biological screen, showed hypotensive and spasmolytic activities[27]. In the follow-up studies the activities were found to be concentrated in the alkaloid fraction. This prompted us to reinvestigates the alkaloidal constituents of the plant which resulted in the isolation of several alkaloids[28]. Of these the isolated protoberberine alkaloids are, capaurine (13), corynoxidine (17), tetrahydropalmatine (14), corydalmine (15) and stepholidine (16), palmatine (18), dehydrocorydalmine (19), jatrorrhizine (20), and stepharanine (21). Most of the alkaloids were known and have been isolated earlier except capaurine (13) and corynoxidine (17), which although known bases, were isolated for the first time from this source.

Capaurine (13) isolated as a minor alkaloid from the chloroform-soluble alkaloid fraction of the ethanolic extract had mass fragmentation pattern characteristic of tetrahydroprotoberberine type of alkaloids. There were two singlet for three protons in the aromatic region. Treatment of the base with an excess of diazomethane yielded *O*-methylcapaurine (13, R_1=OMe). The nmr and other physical data suggested that the compound was *cis*-capaurine.



13 R_1=OH ; R_2=R_3=Me
14 R_1=H ; R_2=R_3=Me
15 R_1=R_2=H ; R_3=Me
16 R_1=R_2=R_3=H

Corynoxidine (17), the other minor tetrahydroprotoberberine alkaloid isolated from the chloroform-soluble fraction, was characterized by physical and spectral data as the *N*-oxide of l-tetrahydropalmatine with a *trans*-B/C ring junction. Corynoxidine has previously been isolated from *Corydalis koidzumiana*[29]. Perbenzoic acid oxidation of dl-tetrahydropalmatine produced dl-corynoxidine. (−)-Tetrahydropalmatine (14), (−)-corydalmine (15), stepholidine (16) were isolated from the chloroform-soluble alkaloid fraction. The quaternary protoberberine alkaloids palmatine (18), dehydrocorydalmine (19), jatrorrhizine (20), and stepharanine (21) were isolated from the n-butanol soluble fraction and were characterized by physical properties, spectroscopic data and direct comparison with an authentic sample.

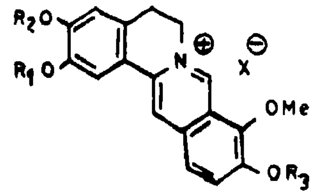


17

There are several reports on the pharmacological properties of the alkaloids of *S. glabra*. Tetrahydropalmatine (14) hydrochloride caused hyperthermia in rats[30]. Palmatine (18) had been found to possess AcTH-like bactericidal and anticholinesterase effects, and it has been concluded that palmatine (18), dl-tetrahydropalmatine and ergot alkaloids have an analogous pharmacological mechanism. Stepharinine (21) has been reported to have antihypertensive properties. Structure-activity relationship has been studied in capaurine (13) for emetine type of activity[31].

According to biogenetic theory[32] the tetrahydroprotoberberine and quaternary protoberberine bases of *S. glabra* could be derived in nature from norlaudanosoline derivatives. Tracer experiments that define the biosynthetic pathways of protoberberine alkaloids of *S. glabra* are as follows. Initial feeding of (L)−[U−^{14}C] tyrosine demostrated that the young plants were actively biosynthesising the tetrahydroprotoberberine alkaloids, stepholidine (16), corydalmine (15), tetrahydropalmatine (13) and the quaternary protoberberine alkaloids palmatine (18), dehydrocorydalmine (19), jatrorrhizine (20) and stepharinine (21). In subsequent experiments the labelled hypothetical precursors were fed to the plants. Feeding of tyrosine in parallel with norlaudanosoline, nor-reticuline, reticuline, nororientaline, protosinomenine and norlaudanidine demonstrated that norlaudanosoline nor-reticuline and reticuline were the only efficient precursors of protoberberine alkaloids. The regiospecificity of labelling in the biosynthetic stepholidine (16) derived from [3−^{14}C] nor-reticuline was shown as follows. Labelled stepholidine was treated with diazomethane to afford radioactiv

tetrahydropalmatine (**14**) which was refluxed with methyl iodide to give radioactive tetrahydropalmatine methiodide with essentially no loss of radioactivity. It was then subjected to Hofmann degradation in the usual way to afford the radioactive methine-I which had essentially the same radioactivity as the parent base. Ozonolysis of the radioactive methine-I yielded radioactive formaldehyde trapped as its dimedone derivative (95% of original the activity). Regioselectivity of label in the biosynthetic tetrahydropalmatine and corydalmine derived from [$3-{}^{14}C$] nor-reticuline were established as above.

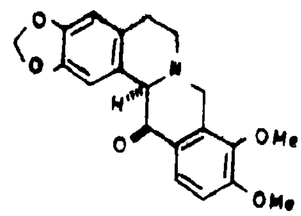


18 $R_1=R_2=R_3=Me$; $X=NO_3$
19 $R_1=R_2=Me$; $R_3=H$; $X=Cl$
20 $R_1=R_3=Me$; $R_2=H$; $X=Cl$
21 $R_1=R_2=H$; $R_3=Me$; $X=Cl$

Carbon atoms 8 in protoberberine alkaloids were derived from *N*-methyl group of reticuline, was shown as follows. *N*-[${}^{14}CH_3$] Reticuline was fed to young plants and biosynthetic protoberberine alkaloids were isolated. The radioactive tetrahydroprotoberberines were separately dehydrogenated with iodine to furnish corresponding quaternary protoberberines. Each of the radioactive quaternary base was then separately degraded to measure the radioactivity at C-8 as described below in the case of biosynthetic palmatine. Labelled palmatine was treated with phenylmagnesium bromide to give the radioactive 8-phenyldihydropalmatine which on chromic acid oxidation (Kuhn-Roth) afforded radioactive benzoic acid (95% of the original activity). The foregoing experiments established that reticuline is a specific precursor of protoberberines in *S. glabra*. The precursors used, however, were racemic. It would be expected that in the biotransformation only one of the two optical isomers should act as a direct substrate. Parallel feedings with (+)-reticuline and (−)-reticuline demonstrated that stereospecificity is maintained in the bioconversion of 1-benzyltetrahydroisoquinoline precursors into protoberberine alkaloids, such as tetrahydropalmatine and palmatine. (+)-Reticuline (**12**) was incorporated about 70 times more efficiently than the (−)-enantiomer. Feeding experiments demonstrated that protoberberinium salts in nature are formed by dehydrogenation of tetrahydroprotoberberines. The rate of their conversion is, however, very different. In some plants both the tetrahydroprotoberberines and their corresponding quaternary protoberberines coexist, for example in *S. glabra* tetrahydropalmatine (**14**) and palmatine (**18**), corydalmine (**15**) and dehydrocorydalmine ; stepholidine (**16**) and stepharinine (**21**) are found in the same plant. The quaternary protoberberines jatrorrhizine, palmatrubine, glabrine and glabrinine also occur in *S. glabra*, however, their corresponding tetrahydroprotoberberines have not yet been isolated.

Tetrahydropalmatine in some plants is found in (+), (−) and (±)-forms. Formation of both the enantiomers in the same plant is of considerable biosynthetic interest. We have studied this aspect of biosynthesis of protoberberine alkaloids and the results are as follows. Tracer experiments with didehydroreticuline demonstrated that the compound is specifically incorporated into (+), − (−) and (±)-tetrahydropalmatines. Feeding of (R)- and (S)-, reticulines separately showed specific incorporation of the enantiomers into (R)- and (S)-, tetrahydropalmatines, respectively. Feeding of [$1-{}^{3}H$, $4'-O-{}^{14}CH_3$] reticuline suggested that reticuline is not converted in the plant into didehydroreticuline and racemisation of optically active forms of tetrahydropalmatine does not take place *via* dehydrotetrahydropalmatine.

Several alkaloids have been isolated by us from the leaves and stems of *Cocculus pendulus*[83] (menispermaceae) in the alcoholic extract of which hypotensive and anticancer activities have been confirmed[84]. Of the isolated bases, the bisbenzylisoquinoline alkaloid, pendulin[85] exhibited hypotensive activity, and cocsulinin[86] was found to be an anticancer agent. During the course of detailed investigation of the alkaloid mixture we isolated a new protoberberine alkaloid, (+)-ophiocarpinone[87]. We have assigned the structure and configuration as shown in **22** for (+)-ophiocarpinone on the basis of spectroscopic data, chemical transformation and CD measurement. A synthesis of (±)-ophicarpinone from berberine has also been achieved.



22

Tetrahydroprotoberberine alkaloids, (−)-sinactine and (±)-sinactine have been isolated from several plant species[88]. (+)-Sinactine (**6**) has been obtained by resolution of (±)-sinactine. However, (+)-sinactine (**6**) as a natural product is isolated for the first time by us from *Corydalis meifolia* Wall[89]. Based on optical rotation (−)-sinactine was suggested to have S-configuration at carbon 13a. (+)-Sinactine (**6**) isolated by us from *Corydalis meifolia* on similar reasoning could have R-configuration at the asymmetric centre. We have confirmed that (+)-sinactine indeed has R-configuration[88] by biosynthetic technique using labelled (R)-, and (S)-, reticulines and by chemical transformation of (+)-sinactine (**6**) into (+)-(R)-tetrahydropalmatine (**14**).

Experiments with labelled 1-benzyltetrahydroisoquinolines and tetrahydroprotoberberine precursors have defined biosynthetic pathways of (+)-sinactine from (R)-reticuline.

In recent years many techniques have been developed to elicit useful and specific information from the mass spectrum of a compound[40]. Chemical ionisation mass spectrometry (CIMS) using ammonia as a reagent gas has emerged as an useful technique because of the softer and selective nature of the isonisation by ammonia[41]. Different classes of compounds such as carbohydrates, peptides, steroids, alkaloids and nitrogen containing compounds have been analysed by this technique. Negative chemical ionisation mass spectrometry (NCIMS)[42] is yet another technique which is gradually gaining acceptance among organic chemists. In order to explore the utility of these techniques in the field of alkaloids, the ammonia CIMS of some tetrahydroprotoberberine alkaloids, coreximine, stepholidine (**16**), corydalmine (**15**), tetrahydropalmatine (**14**), sinactine (**6**), cavidine (**7**) and stylopine (**10**) have been examined by us under both positive and negative ionisation techniques[29].

Since alkaloids are sufficiently basic to remove a proton from NH_4^+, protonated molecular ions give rise to the most intense peaks in the spectra of these compounds. As expected no NH_4^+ adduct ions are observed. The preferred site of protonation will be the nitrogen atom of the quinolizidine system. Protoberberines which have hydroxylic function show loss of H_2O from the $(M^+-H)^+$ ions, presumably protonated on the hydroxyl oxygen. The other peaks in the spectra of the tetrahydroprotoberberines corresponded to retro-Diels-Alder fragments. In the negative chemical ionisation mass spectrometry the reactant gas can have three functions, (i) showing down the primary high energy electrons to give thermal electrons, (ii) charge transfer when the electron affinity of the reactant gas is less than that of the substance, and (iii) true chemical ionization where ionization occurs as a result of ion molecular reaction. The first two processes lead to resonance electron capture with or without dissociation of the molecule. The use of gases, such as CH_4, $i-C_4H_{10}$, NH_3 and H_2 results in the formation of low energy electrons. $(M-H)^-$ ion is usually observed when NH_3 is used as the enhancement gas. None of the tetrahydroprotoberberine alkaloids when subjected to NCI gives stable molecular anions. This is understandable as these molecules do not contain any electron capturing groups. However, all the compounds show $(M-H)^-$ ions presumably formed by dissociative electron capture. Tetrahydroprotoberberine alkaloids containing hydroxyl function give very intense $(M-H)^-$ ions (83-56%). Loss of the phenolic hydrogen will be relatively easy as it results in the formation of resonance stabilised phenoxide anion. The results of positive and negative chemical ionisation mass spectra of tetrahydroprotoberberine alkaloids using ammonia as the reagent gas show the complementary nature of positive and negative ion mass spectra.

Acknowledgement

The author is grateful to his students Dr. (Miss) Sudha Jain, Drs. Sandeep Gupta, P. K. Gupta and P. P. Joshi for the participation in the programme and to Dr. K. P. Madhusudanan for mass spectral studies.

References

1. K. Mehra, H. S. Garg, D. S. Bhakuni and N. M. Khanna, *Indian J. Chem., Sect. B*, 1976, **14**, 844.
2. O. E. Edwards and K. L. Handa, *Can. J. Chem.*, 1961, **39**, 1801.
3. R. N. Chopra, S. L. Nayar and I. C. Chopra, "Glossary of Medicinal Plants", C.S.I.R., New Delhi, 1959, p. 78.
4. F. Bohlmann, *Ber. Deut. Chem. Ges.*, 1958, **91**, 2157.
5. M. Shamma, M. J. Hillman and C. D. Jones, *Chem. Rev.*, 1969, **69**, 779.
6. M. Corrodi and E. Hardegger, *Helv. Chim. Acta*, 1956, **39**, 889.
7. C. Y. Chen and D. B. MacLean, *Can. J. Chem.*, 1968, **46**, 2501.
8. M. A. Rau, "High Altitude Flowering Plants", Botanical Survey of India, Howrah, 1975, p. 66.
9. K. R. Kirtikar and B. D. Basu, "Indian Medicinal Plants", L. M. Basu, Allahabad, 1933, Vol. 1, p. 135.
10. R. C. Anderson and K. K. Chen, *Fed. Proc.*, 1946, **5**, 163.
11. B. N. Dhawan, M. P. Dubey, B. N. Mehrotra, R. P. Rastogi and J. S. Tandon, *Indian J. Exptl. Biol.*, 1980, **18**, 594.
12. H. Taguchi and I. Imaseki, *J. Pharm. Soc. Jpn.*, 1963, **83**, 578.
13. I. A. Israilov, M. S. Yunusov and S. Y. Yunusov, *Khim. Prir. Soedin.*, 1979, **3**, 418.
14. C. K. Yu, D. B. MacLean, R. G. A. Rodrigo and R. H. F. Manske, *Can. J. Chem.*, 1970, **48**, 3673.
15. P. W. Jeffs, *Experientia*, 1965, **21**, 690.
16. K. Goto and Z. Kitasato, *J. Chem. Soc.*, 1930, 1234.
17. N. M. Mollov and G. I. Yakimov, *Dokl. Bolg. Akad. Nauk*, 1972, **25**, 59.
18. S. Pfeifer and V. Hanus, *Pharmazie*, 1965, **20**, 394.
19. H. Haguchi and I. Imaseki, *J. Pharm. Soc. Jpn.*, 1964, **84**, 773.
20. E. Spath and P. L Julian, *Chem. Ber.*, 1931, **64**, 1131.
21. R. H. F. Manske and W. R. Ashford in "The Alkaloids", eds. R. H. F. Manske and H. L. Hlmes, Academic Press, New York, 1954, Vol. 4, p. 102.
22. R. H. F. Manske, *Can. J. Res., Sect. B*, 1936, **14**, 325.
23. A. R. Battersby, M. Hirst, D. J. McCaldin, R. Southgate and J. Staunton, *J. Chem. Soc.*, (C), 1968, 2163.
24. A. R. Battersby, J. Staunton, H. R. Wiltshire, R. J. Francis and R. Southgate, *J. Chem. Soc., Perkin Trans. I*, 1975, 1147.
25. H. L. Holland, M. Castillo, D. B. MacLean and I. D. Spenser, *Can. J. Chem.*, 1974, **52**, 2818.
26. K. R Kirtikar and B. D. Basu, "Indian Medicinal Plants", L. M. Basu, Allahabad, 1933, p. 94.
27. M. L. Dhar, M. M. Dhar, B. N. Dhawan, B. N. Mehrotra and C. Ray, *Indian J. Exptl. Biol.*, 1968, **6**, 232.
28. D. S. Bhakuni and S. Gupta, *J. Nat. Prod.*, 1982, **45**, 407.
29. C. Tani, N. Nagakura, S. Hattori and N. Masaki, *Chem. Lett.*, 1975, 1081.
30. N. K. Khanna, B. R. Madan, O. P. Mahatma and S. C. Surana, *J. Med. Res.*, 1972, **60**, 472.
31. R. S. Gupta, J. J. Krepinsky and L. Siminovitch, *Mol. Pharmacol.*, 1980, **18**, 136.
32. R. Robinson, "The Structural Relation of Natural Products", Clarendon Press, Oxford, 1955, p. 78.
33. D. S. Bhakuni and P. P. Joshi, *Tetrahedron*, 1975, **31**, 2575.

34. D. S. BHAKUNI, M. M. DHAR, B. N. DHAWAN and B. N. MEHROTRA, *Indian J. Exptl. Biol.*, 1969, **7**, 250.
35. N. C. GUPTA, D. S. BHAKUNI and M. M. DHAR, *Experientia*, 1970, **26**, 12.
36. P. P. JOSHI, D. S. BHAKUNI and M. M. DHAR, *Indian J. Chem., Sect. B*, 1974, **12**, 517.
37. D. S. BHAKUNI, P. K. GUPTA, P. P. JOSHI and S. GUPTA, *Indian J. Chem., Sect. B*, 1982, **21**, 389.
38. D. S. BHAKUNI, S. JAIN and S. GUPTA, *Tetrahedron*, 1983, **19**, 455.
39. D. S. BHAKUNI and R. CHATURVEDI, unpublished work.
40. U. P. SCHLUNEGGER, *Top. Curr. Chem.*, 1981, **95**, 49.
41. T. KEOUGH and A. DESTEFANO, *J. Org. Mass Spectrom.*, 1981, **16**, 527 ; B. R. DEMARK and P. D. KLEIN, *J. Lipid Res.*, 1981, **22**, 166.
42. R. C. DOUGHERTY, *Anal. Chem.*, 1981, **53**, 625 A.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1023-1027

A Facile Synthesis of 4-Propyl-psoralene and Angelicin Derivatives

V. K. AHLUWALIA* and R. P. TRIPATHI

Department of Chemistry, University of Delhi, Delhi-110 007

7-Hydroxy-4-propyl-2*H*-1-benzopyran-2-one (1) on allylation followed by Claisen migration of the intermediate allyloxycoumarin 2 with *N,N*-dimethylaniline gives 8-allyl- and 6-allyl-7-hydroxy-4-propyl-2*H*-1-benzopyran-2-ones (3 and 4) which on oxidation with OsO_4-KIO_4 and subsequent cyclodehydration with PPA yield 7-propyl-5*H*-furo[2,3-h][1]benzopyran-5-one (7) and 5-propyl-7H-furo[3,2-g][1]benzopyran-7-one (10), respectively. However, these allyl coumarins 3 and 4 on cyclisation with sulphuric acid followed by dehydrogenation with DDQ afford 2-methyl-7-propyl-5*H*-furo[2,3-h][1]benzopyran-5-one (9) and 2-methyl-5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one (12) respectively. Similarly, 9-methyl-5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one (16) and 2,9-dimethyl-5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one (18) are synthesised starting from 7-hydroxy-8-methyl-4-propyl-2*H*-1-benzopyran-2-one (13).

THE natural occurrence[1-4], photodynamic activity[5,6] of psoralene and angelicin derivatives and insecticidal properties[7] of 4-propylcoumarins prompted us to devise a convenient method for the synthesis of 4-propyl angelicins and psoralenes. Different methods[8-18] have been used for the synthesis of psoralene and angelicin derivatives. But no considerable efforts have so far been made for the synthesis of 4-propyl angelicins and psoralenes. In the present communication, synthesis of 4-propyl angelicin and psoralene derivatives, *viz.* **7**, **9**, **10**, **12**, **16** and **18** has been described.

Results and Discussion

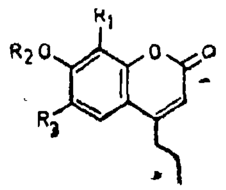
7-Hydroxy-4-propyl-2*H*-1-benzopyran-2-one (**1**)[17] on allylation with allylbromide in acetone and anhydrous potassium carbonate gave 7-allyloxy-4-propyl-2*H*-1-benzopyran-2-one (**2**) which on Claisen migration with *N,N*-dimethylaniline afforded a mixture of two products, *viz.* 8-allyl-7-hydroxy-4-propyl-2*H*-1-benzopyran-2-one (**3**) (60%) and 6-allyl-7-hydroxy-4-propyl-2*H*-1-benzopyran-2-one (**4**) (10%). The 6-allyl isomer was obtained exclusively (60%) by allylation of 7-hydroxy-8-iodo-4-propyl-2*H*-1-benzopyran-2-one (**5**) (which was obtained by iodination of **1** with iodine and periodic acid in ethanol) to give 7-allyloxy-8-iodo-4-propyl-2*H*-1-benzopyran-2-one (**6**) and subsequent Claisen migration with *N,N*-dimethylaniline.

The above allylcoumarin **3** on oxidation with OsO_4-KIO_4 followed by cyclodehydration with PPA of the intermediate acetaldehyde derivative gave 7-propyl-5*H*-furo[2,3-h][1]benzopyran-5-one (**7**) (4-propylangelicin). Its structure was established on the basis of elemental analysis, ir spectrum 1720 (C=O), 1620 and 1610 (C=C) and 1050, 770 cm^{-1} (furan ring), and ^1H nmr spectrum which showed two doublets *ortho*-coupled (J 9.5 Hz) at δ 7.35 and 7.25 for H-8 and H-9, and one doublet (J 2.5 Hz) at δ 6.88 for H-3 along with other usual signals. However, **3** on trituration with concentrated sulphuric acid gave 2,3-dihydro-2-methyl-7-propyl-5*H*-furo[2,3-h][1]benzopyran-5-one (**8**) which on dehydrogenation with DDQ yielded 2-methyl-7-propyl-5*H*-furo[2,3-h][1]benzopyran-5-one (**9**). Its structure was in good agreement with its ir and nmr data (see experimental). Similarly, oxidation of **4** with OsO_4-KIO_4 followed by cyclodehydration with PPA yielded a product which was assigned the structure as 5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one (**10**) on the basis of its ir spectrum 1720 (C=O), 1628 and 1575 cm^{-1} (C=C) and 1105, 785 cm^{-1} (furan ring), and ^1H nmr spectrum which displayed two singlets at δ 7.41 and 7.78 for *para* H-9 and H-4 and a doublet ($J_{2,3}$ 2.5 Hz) for H-3. Trituration of **4** with concentrated sulphuric acid gave 2,3-dihydro-2-methyl-5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one (**11**). Its dehydrogenation with DDQ afforded 2-methyl-5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one (**12**). This structure was in conformity with its ir and nmr data (see experimental).

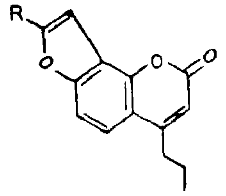
Similarly, 7-hydroxy-8-methyl-4-propyl-2*H*-1-benzopyran-2-one (**13**) (obtained by Pechman condensation of 1,3-dihydroxy-2-methylbenzene with ethylbutyrylacetate) on allylation with allyl bromide gave 7-allyloxy-8-methyl-4-propyl-2*H*-1-benzopyran-2-one (**14**) which on Claisen migration gave only 6-allyl-8-methyl-4-propyl-2*H*-1-benzopyran-2-one (**15**) (70%). **15** on oxidation with OsO_4-KIO_4 and subsequent cyclodehydration afforded 5-propyl-9-methyl-7*H*-furo[3,2-g][1]benzopyran-7-one (**16**). Its structure was in good agreement with its spectral data (see experimental). However, trituration of **14** with concentrated sulphuric acid followed by dehydrogenation, of the formed 2,9-dimethyl-2,3-dihydro-5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one (**17**) with

DDQ yielded 2,9-dimethyl-5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one (**18**).

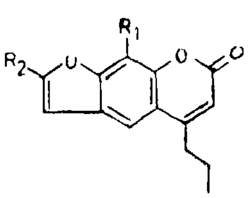
DDQ was used earlier[16] for the dehydrogenation of dihydrofuranocoumarins. It has not been used for the dehydrogenation of 2-methyldihydrofuranocoumarins possibly due to the presence of methyl group. However, in the present investigation DDQ has been used successfully for the dehydrogenation of 2-methyldihydrofuranocoumarins **8**, **11** and **17**.



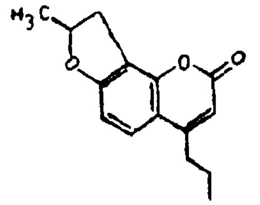
1 $R_1=R_2=R_3=H$
2 $R_1=R_3=H$, $R_2=CH_2-CH=CH_2$
3 $R_1=CH_2CH=CH_2$, $R_2=R_3=H$
4 $R_1=R_2=H$, $R_3=CH_2CH=CH_2$
5 $R_1=I$, $R_2=R_3=H$
6 $R_1=I$, $R_2=CH_2CH=CH_2$, $R_3=H$
13 $R_1=CH_3$, $R_2=R_3=H$
14 $R_1=CH_3$, $R_2=CH_2CH=CH_2$, $R_3=H$
15 $R_1=CH_3$, $R_2=H$, $R_3=CH_2-CH=CH_2$



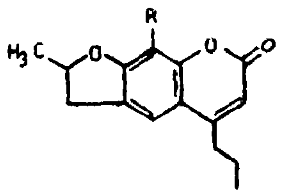
7 R=H
9 $R=CH_3$



10 $R_1=R_2=H$
12 $R_1=H$, $R_2=CH_3$
16 $R_1=CH_3$, $R_2=H$
18 $R_1=R_2=CH_3$



8



11 R=H
17 $R=CH_3$

Experimental

All melting points are uncorrected. Ir spectra were determined in KBr with a Perkin-Elmer 598 spectrophotometer. Nmr spectra were run in $CDCl_3$ on a Perkin-Elmer R-32 (90 MHz) with TMS as the internal standard. Anhydrous sodium sulphate was used as drying agent.

*7-Allyloxy-4-propyl-2*H*-1-benzopyran-2-one* (**2**) : A solution of 7-hydroxy-4-propyl-2*H*-1-benzopyran-2-one (**1**)[17] (1 g) in dry acetone (75 ml) was refluxed with allyl bromide (0.3 ml) in presence of anhydrous potassium carbonate (3 g) for 5-6 h. The solution was filtered, solvent distilled off and the residue treated with the crushed ice to give **2** (0.9 g, 78%). It was crystallised from benzene-petroleum ether as colourless prisms, m.p. 55-6° (Found : C, 73.7 : H, 6.5. $C_{15}H_{16}O_3$ requires C, 73.5 ; H, 6.2%) ; δ ($CDCl_3$) 1.02 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.70 (2H, m, $CH_3CH_2CH_2$), 2.65 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 4.52 (2H, d, *J* 5.5 Hz, $OCH_2CH=CH_2$), 5.31 (2H, m, $OCH_2-CH=CH_2$), 5.90 (1H, m, $OCH_2CH=CH_2$), 6.01 (1H, s, H-3), 6.75 (2H, dd, *J* 9.5 Hz, 2.5 Hz, H-6 and H-8) and 7.40 (1H, d, *J* 9.5 Hz, H-5).

*Claisen migration of 7-allyloxy-4-propyl-2*H*-1-benzopyran-2-one. Formation of 8-allyl-7-hydroxy-4-propyl-2*H*-1-benzopyran-2-one* (**3**) *and 6-allyl-7-hydroxy-4-propyl-2*H*-1-benzopyran-2-one* (**4**) : The above allyloxy coumarin (**2**) (0.5 g) was refluxed with *N,N*-dimethylaniline (5 ml) for 6 h. The reaction mixture was cooled and poured over ice-cold hydrochloric acid. The separated product was treated with sodium hydroxide solution (5%) and the solution filtered. The filtrate on acidification yielded a mixture of two products which were separated by column chromatography over silica gel. Elution of the column (i) with benzene-petroleum ether (1 : 1) gave 8-allyl-7-hydroxy-4-propyl-2*H*-1-benzopyran-2-one (**3**) and (ii) with benzene afforded 6-allyl-7-hydroxy-4-propyl-2*H*-1-benzopyran-2-one (**4**).

3 crystallised from ethanol as shining rectangular plates (0.3 g, 60%), m.p. 112-3° (Found : C, 73.8 ; H, 6.5. $C_{15}H_{16}O_3$ requires C, 73.7 ; H, 6.5%) ; its acetate prepared (Ac_2O/C_5H_5N) melted at 85-6° ; δ ($CDCl_3$) 1.06 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.60 (2H, m, $CH_3CH_2CH_2$), 2.30 (3H, s, $CO-CH_3$), 2.71 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 3.51 (2H, d, *J* 7 Hz, $CH_2-CH=CH_2$), 5.08 (2H, m, $CH_2-CH=CH_2$), 5.85 (1H, m, $CH_2-CH=CH_2$), 6.22 (1H, s, H-3), 6.98 and 7.49 (each 1H, each d, *J* 9.5 Hz, H-6 and H-5, respectively).

4 crystallised from methanol as colourless plates (0.05 g, 10%), m.p. 140° (Found : C, 73.6 ; H, 6.2. $C_{15}H_{16}O_3$ requires C, 73.7 ; H, 6.5%) ; δ ($CDCl_3$) 1.10 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.70 (2H, m, $CH_3CH_2CH_2$), 2.70 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 3.45 (2H, d, *J* 7 Hz, $CH_2CH=CH_2$), 5.05 (2H, m, $CH_2CH=CH_2$), 5.95 (1H, m, $CH_2CH=CH_2$), 6.01, 7.10 and 7.30 (each 1H, each s, H-3, H-8 and H-5, respectively).

*7-Hydroxy-8-iodo-4-propyl-2*H*-1-benzopyran-2-one* (**5**) : 7-Hydroxy-4-propyl-2*H*-1-benzopyran-2-one (**1**) (2 g) was dissolved in minimum amount of alcohol, and to the solution iodine (1.3 g) and periodic acid (0.56 g) in water were added. The mixture was stirred for 2 h at room temperature and then diluted with water. A solid separated was filtered, washed with water, dried and crystallised from ethanol as colourless plates (2.4 g, 76%), m.p. 213-4° (Found : C, 43.5 ; H, 3.3. $C_{12}H_{11}IO_3$ requires C, 43.6 ; H, 3.2%) ; its acetate (Ac_2O/C_5H_5N) melted at 148-9° ; δ ($CDCl_3$) 1.05 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.65 (2H, m, $CH_3CH_2CH_2$), 2.32 (3H, s, $CO-CH_3$), 2.69 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 6.20 (1H, s, H-3), 7.05 and 7.55 (each 1H, each d, *J* 9.5 Hz, H-6 and H-5, respectively).

*7-Allyloxy-8-iodo-4-propyl-2*H*-1-benzopyran-2-one* (**6**) : The above coumarin (**5**) (2 g) in dry acetone was refluxed with allyl bromide (0.30 ml) in presence of anhydrous K_2CO_3 for 6 h. Working up of the reaction mixture as above gave **6**. It crystallised from methanol as light yellow needles (1.65 g, 75%), m.p. 139-40° (Found : C, 48.4 ; H, 4.1. $C_{15}H_{15}IO_3$ requires C, 48.5 ; H, 4.0%) ; δ ($CDCl_3$) 1.08 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.65 (2H, m, CH_3CH_2-CH_2), 2.61 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 4.52 (2H, d, *J* 7 Hz, $OCH_2CH=CH_2$), 5.30 (2H, m, $OCH_2-CH=CH_2$), 5.85 (1H, m, $OCH_2CH=CH_2$), 6.01 (1H, s, H-3), 6.75 and 7.55 (each 1H, each d, *J* 9.5 Hz, H-6 and H-5, respectively).

Claisen migration of **6**. *Formation of* (**4**) : The above allyloxy coumarin (**6**) (0.5 g) was refluxed with *N,N*-dimethylaniline for 6 h. Working up of the reaction mixture as above and crystallisation from ethanol gave a product which was identical in all respects (m.p., m.m.p., ir and nmr) to the coumarin, 6-allyl-7-hydroxy-4-propyl-2*H*-1-benzopyran-2-one (**4**) obtained above.

*7-Propyl-5*H*-furo[2,3-h][1]benzopyran-5-one* (**7**) : Allyl coumarin (**3**) (0.25 g) in ethyl acetate (80 ml) with an equal volume of water was stirred with OsO_4 (0.06 g). The mixture was shaken for 1.5 h and during the period potassium periodate (2 g) was added in small lots. The reaction mixture was stirred for 2 h more. The ethyl acetate layer was separated and aqueous solution extracted with more ethyl acetate. The combined ethyl acetate layer was washed well with water, dried and distilled. The residue consisting of acetaldehyde derivative was heated on boiling water bath with polyphosphoric acid (10 ml) for 20 min and then poured over crushed ice. The separated solid was taken up in ether, the ethereal layer washed successively with Na_2CO_3 solution (5%), water, dried and then distilled. The residue on crystallisation from benzene-petroleum ether gave colourless plates of (**7**) (0.14 g, 60%), m.p. 163-4° (Found : C, 73.2 ; H, 5.0. $C_{14}H_{12}O_3$ requires C, 73.6 ; H, 5.2%). ν_{max} (KBr) 1720 (C=O), 1620 and 1610 (C=C) and 1050, 768 cm^{-1} (furan ring) ; δ ($CDCl_3$) 1.01 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.70 (2H, m, $CH_3CH_2CH_2$), 2.60 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 6.09 (1H, s, H-6), 6.98 (1H, d, *J* 2.5 Hz, H-3), 7.15 and 7.35 (each 1H, d, *J* 9.5 Hz, H-9 and H-8, respectively) and 7.47 (1H, d, *J* 2.5 Hz, H-2).

*2,3-Dihydro-2-methyl-7-propyl-5*H*-furo[2,3-h] [1] benzopyran-5-one* (**8**) : Allyl coumarin (**3**) (0.5 g) was triturated with concentrated sulphuric acid (10 ml) for 15 min. The reaction mixture was poured over crushed ice. The product was filtered, and washed with NaOH solution (5%) and finally with water. **8** was crystallised from benzene-petroleum ether as colourless needles (0.35 g, 70%), m.p. 97-8° (Found : C, 73.4 ; H, 6.6. $C_{15}H_{16}O_3$ requires C, 73.6 ; H, 6.8%) ; ν_{max} (KBr) 1710 (C=O), 1610, 1575 (C=C), 1100, 1060 cm^{-1} (furan ring) ; δ ($CDCl_3$) 1.10 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.50 (3H, d, *J* 7 Hz, 2-CH_3), 1.70 (2H, m, $CH_3CH_2CH_2$), 2.71 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 3.0-3.70 (2H, m, H-3), 5.10 (1H, m, H-1), 6.10 (1H, s, H-6), 6.75 and 7.45 (each 1H, each d, *J* 2.5 Hz, H-9 and H-8, respectively).

*2-Methyl-7-propyl-5*H*-furo[2,3-h] [1] benzopyran-5-one* (**9**) : Coumarin (**8**) (0.1 g) was refluxed with DDQ (0.1 g) in anhydrous benzene (10 ml) for 72 h. The solution was filtered, washed successively with Na_2CO_3 solution (10%), water, dried and distilled. The residue, thus obtained was subjected to column chromatography over silica gel. Elution of the column with benzene-petroleum ether (1 : 1) gave **9** which crystallised from benzene-petroleum ether as rectangular plates (0.06 g, 60%), m.p. 114-5° (Found : C, 74.3 ; H, 5.7. $C_{15}H_{14}O_3$ requires C, 74.3 ; H, 5.7%) ; ν_{max} (KBr) 1720 (C=O), 1610, 1598 (C=C), 1098, 775 cm^{-1} (furan ring) ; δ ($CDCl_3$) 1.05 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.72 (2H, m, $CH_3CH_2CH_2$), 2.48 (3H, s, 2-CH_3), 2.71 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 6.10 and 6.60 (each 1H, each s, H-6 and H-3, respectively), 7.20 and 7.32 (each 1H, each d, *J* 9.5 Hz, H-9 and H-8, respectively).

*5-Propyl-7*H*-furo[3,2-g][1]benzopyran-7-one* (**10**) : Allyl coumarin (**4**) (0.25 g) in ethyl acetate (80 ml) containing an equal volume of water was stirred with OsO_4 (0.06 g). The mixture was shaken for 1.5 h and during the period KIO_4 (2 g) added in small lots. The reaction mixture was stirred for 2 h more. Working up of the reaction mixture as above gave **10** which crystallised from benzene-petroleum ether as shining rectangular plates (0.14 g, 60%), m.p. 128-9° (Found : C, 73.3 ; H, 5.3. $C_{14}H_{12}O_3$ requires C, 73.6 ; H, 5.2%) ; ν_{max} (KBr) 1710 (C=O), 1625, 1575 (C=C), 1105, 785 cm^{-1} (furan ring) ; δ ($CDCl_3$) 1.15 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.80 (2H, m, $CH_3CH_2CH_2$), 2.85 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 6.22 (1H, s, H-6), 6.80 (1H, d, *J* 2.5 Hz, H-3), 7.42 (1H, s, H-9), 7.63 (1H, d, *J* 2.5 Hz, H-2) and 7.80 (1H, s, H-4).

*2,3-Dihydro-2-methyl-5-propyl-7*H*-furo[3,2-g][1] benzopyran-7-one* (**11**) : Trituration of **4** (0.5 g) with concentrated sulphuric acid (10 ml) for 15 min and working up of the reaction mixture as above gave a solid which crystallised from benzene-petroleum ether as colourless needles (0.35 g, 70%), m.p. 115-6° (Found : C, 73.6 ; H, 5.5. $C_{15}H_{16}O_3$ requires C, 73.5 ; H, 5.2%). ν_{max} (KBr) 1705 (C=O), 1620, 1580 (C=C), 1110 and 1090 cm^{-1} (furan ring) ; δ ($CDCl_3$) 1.10 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.49 (3H, d, *J* 7 Hz, 2-CH_3), 1.75 (2H, m, $CH_3CH_2CH_2$), 2.69 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 2.89-3.50 (2H, m, H-3), 5.01 (1H, m, H-2), 6.05, 6.65 and 7.31 (each 1H, each s, H-6, H-9 and H-5, respectively).

*2-Methyl-5-propyl-7*H*-furo[3,2-g] [1]benzopyran-7-one* (**12**) : Coumarin (**11**) (0.1 g) was refluxed with DDQ (0.1 g) in anhydrous benzene (10 ml) for 72 h. Working up of the reaction mixture as above gave **12** which crystallised from benzene-petroleum ether as colourless needles (0.06 g, 60%),

m.p. 140° (Found : C, 74.2 ; H, 5.7. $C_{15}H_{14}O_3$ requires C, 74.4 ; H, 5.7%). ν_{max} (KBr) 1720 (C=O), 1610, 1575 (C=C), 1100, 810 cm^{-1} (furan ring) ; δ ($CDCl_3$) 1.09 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.79 (2H, m, $CH_3CH_2CH_2$), 2.49 (3H, s, 2-CH_3), 2.79 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 6.27, 6.49, 7.40 and 7.22 (each 1H, each s, H-6, H-8, H-3 and H-5, respectively).

*7-Hydroxy-8-methyl-4-propyl-2*H*-1-benzopyran-2-one* (**13**) : A mixture of 1,3-dihydroxy-2-methylbenzene (10 g) and ethyl butyrylacetate (9.2 ml) was cooled (0-5°) in an ice bath and concentrated sulpruric acid (25 ml) was added gradually with shaking. The yellow oil, thus obtained, was kept in refrigerator for 24 h and then poured over crushed ice with constant stirring. The separated solid was filtered, washed with water, dried and crystallised from ethanol as colourless needles (15.8 g, 90%), m.p. 165-6° (Found : C, 72.4 ; H, 5.2. $C_{13}H_{14}O_3$ requires C, 72.2 ; H, 5.5%) ; its acetate prepared (Ac_2O/C_5H_5N) melted at 106-7° ; δ ($CDCl_3$) 1.09, (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.75 (2H, m $CH_3CH_2CH_2$), 2.30 (3H, s, CO−CH_3) ; 2.40 (3H, s, 8-CH_3), 2.80 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 6.23 (1H, s, H-3), 7.02 and 7 50 (each 1H, each d, *J* 9.5 Hz, H-6 and H-5, respectively).

*7-Allyloxy-8-methyl-4-propyl-2*H*-1-benzopyran-2-one* (**14**) : A solution of coumarin (**13**) (1 g) in dry acetone (75 ml) was refluxed with allyl bromide (0.32 ml) in presence of anhydrous K_2CO_3 (3.0 g) for 6 h. Working up of the reaction mixture as above gave **14** which crystallised from benzene-petroleum ether as shining prisms (0.9 g, 80%), m.p. 80-81° (Found : C, 75.2 ; H, 6.7. $C_{16}H_{18}O_3$ requires C, 75.6 ; H, 6.9%) ; δ ($CDCl_3$) 1.01 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.70 (2H, m, $CH_3CH_2CH_2$), 2.30 (3H, s, 8-CH_3), 2.70 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 4.10 (2H, d, *J* 7 Hz, OCH_2CH-CH_2), 5.42 (2H, t, *J* 7 Hz, $OCH_2-CH=CH_2$), 5.80 (1H, m, $OCH_2-CH=CH_2$). 6.09 (1H, s, H-3), 6.85 and 7.45 (each 1H, each d, *J* 9.5 Hz, H-6 and H-5, respectively).

*6-Allyl-7-hydroxy-8-methyl-4-propyl-2*H*-1-benzopyran-2-one* (**15**) : Allyloxy coumarin (**14**) (0.5 g) was refluxed with *N,N*-dimethylaniline (5 ml) for 6 h. Working up of the reaction mixture as above gave **15** which crystallised from ethanol as colourless needles (0.35 g, 70%), m.p. 124-5° (Found : C, 75.8 ; H, 6.5. $C_{16}H_{18}O_3$ requires C, 75.6 ; H, 6.9%) ; its acetate prepared (Ac_2O/C_5H_5N) melted at 91-2° ; δ ($CDCl_3$) 1.00 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.65 (2H, m, $CH_3CH_2CH_2$), 2.20 (3H, s, CO−CH_3), 2.32 (3H, s, 8-CH_3), 2.70 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 3.25 (2H, d, *J* 7 Hz, $CH_2CH=CH_2$), 5.01 (2H, m, $CH_2-CH=CH_2$), 5.80 (1H, m, $CH_2-CH=CH_2$), 6.12 and 7.32 (each 1H, each s, H-3 and H-5, respectively).

*9-Methyl-5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one* (**16**) : Coumarin (**15**) (0.25 g) in ethyl acetate (80 ml) containing an equal volume of water was stirred with OsO_4 (0.06 g) for 1.5 h and during the period potassium periodate (2 g) added in small lots. The reaction mixture was stirred for 2 h more and worked up as above to give **16** which crystallised from benzene-petroleum ether as colourless needles (0.14 g, 60%), m.p. 133-4° (Found : C, 75.0 ; H, 6.1. $C_{16}H_{18}O_3$ requires C, 74.8 ; H, 5.9%) ; ν_{max}(KBr) 1710 (C=O), 1590 (C=C) and 1080, 760 cm^{-1} (furan ring) ; δ ($CDCl_3$) 1.10 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.70 (2H, m, $CH_3CH_2CH_2$), 2.50 (3H, s, 8-CH_3), 2.80 (2H, t. *J* 7 Hz, $CH_3CH_2CH_2$), 6.15 (1H, s, H-6), 6.70 (1H, d, *J* 2.5 Hz, H-3) and 7.60 (2H, m, H-2 and H-4).

*2,3-Dihydro-2,9-dimethyl-5-propyl-7*H*-furo[3,2-g]-[1]benzopyran-7-one* (**17**) : 6-Allyl-7-hydroxy-8-methyl-4-propyl-2*H*-1-benzopyran-2-one (**15**) (0.5 g) was triturated with concentrated sulphuric acid (20 ml) for 15 min and working up of the reaction mixture as above gave **17** which crystallised from benzene-petroleum ether as colourless needles (0.35 g, 70%), m.p. 140-1° (Found : C, 75.4 ; H, 6.8. $C_{16}H_{18}O_3$ requires C, 75.6 ; H, 6.9%) ; ν_{max} (KBr) 1720 (C=O), 1620, 1580 (C=C) and 1100, 1090 cm^{-1} (furan ring) ; δ ($CDCl_3$) 1.10 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.50 (3H, d, *J* 7 Hz, 2-CH_3), 1.65 (2H, m, $CH_3CH_2CH_2$), 2.30 (3H, s, 9-CH_3), 2.70 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 2.90-3.50 (2H, m, H-3), 5.01 (1H, m, H-2), 6.10 and 7.30 (each 1H, each s, H-6 and H-5, respectively).

*2,9-Dimethyl-5-propyl-7*H*-furo[3,2-g][1]benzopyran-7-one* (**18**) : A solution of coumarin (**17**) (0.1 g) was refluxed with DDQ (0.1 g) in anhydrous benzene (10 ml) for 56 h and working up of the reaction mixture as above gave **18** which crystallised from benzene-petroleum ether as colourless plates (0.06 g, 60%), m.p. 165-6° (Found : C, 72.2 ; H, 6.3. $C_{16}H_{16}O_3$ requires C, 75.4 ; H, 6.1%) ; ν_{max} (KBr) 1710 (C=O), 1610, 1585 (C=C), 1050, 760 cm^{-1} (furan ring) ; δ ($CDCl_3$) 1.10 (3H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 1.70 (2H, m, $CH_3CH_2CH_2$), 2.50 and 2.58 (each 3H, each s, 2- and 9-CH_3), 2.80 (2H, t, *J* 7 Hz, $CH_3CH_2CH_2$), 6.19, 6.40 and 7.53 (each 1H, each s, H-6, H-3 and H-4, respectively).

Acknowledgement

The authors thank the U.G.C., New Delhi for financial assistance.

References

1. F. M. DEAN, "Naturally Occurring Oxygen Ring Compounds", London, Butterworths, 1963, p. 198.
2. R. D. H. MURRAY, *Fortschr., Chem. Org. Naturst.*, 1978, **35**, 199.
3. K. D. KAUFMAN, *J. Org. Chem.*, 1961, **26**, 117.
4. R. ANEJA, S. K. MUKHERJEE and T. R. SESHADRI, *Tetrahedron*, 1958, **4**, 286.
5. G. CAPORALE, L. MUSAJOE, G. RODIGHERO, F. BACCICHETTI, *Experientia*, 1967, **23**, 985.
6. M. A. PATHAK, J. H. FELLMAN and K. D. KAUFMAN, *J. Invest. Derm.*, 1960, **35**, 165 ; 1967, **48**, 103.
7. C. DJERRASI and B. E. J. GILBERT, *J. Am. Chem. Soc.*, 1958, **80**, 3686 ; R. A. FINNEGAN and B. GILBERT, *Tetrahedron Lett.*, 1959, **1**, 10.
8. E. SPATH, B. L. MANJUNATH, M. PAILER and H. S. JOIS, *Ber. Deut. Chem. Ges.*, 1936, **69**, 1087.
9. R. A. FOSTER, A. ROBERTSON and A. BUSHRA, *J. Chem. Soc.*, 1948, 2254.

10. E. C. HORNING and D. B. REINER, *J. Am. Chem. Soc.*, 1948, **70**, 3619 ; 1950, **72**, 1514.
11. T. R. SESHADRI and M. S. SOOD, *Indian J. Chem.*, 1963, **1**, 291.
12. D. K. CHATTERJEE and K. SEN, *Sci. Cult.*, 1967, **33**, 528.
13. L. R. WARDEN, K. D. KAUFMAN, J. A. WEIS and T. K. SCHAAF, *J. Org. Chem.*, 1969, **34**, 2311.
14. N. H. PARDANANI and K. M. TRIVEDI, *Aust. J. Chem.*, 1972, **25**, 1537.
15. A. ROY, A. D. GUPTA and K. SEN, *Indian J. Chem.*, 1974, **12**, 564.
16. K. R. SHAH and K. N. TRIVEDI, *Aust. J. Chem.*, 1974, **27**, 1971.
17. N. G. KOTWANI, S. M. SETHNA and C. D. ADVANI, *Proc. Indian Acad. Sci., Sect. A*, 1942, **15**, 441.
18. M. NAKAYAMA, S. FUJIMATO, K. FUKUI and J. K. MACLEOD, *Aust. J. Chem.*, 1971, **24**, 209.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1028-1031

Synthesis in 3-Azafluorene Group. Part-III

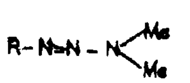
J. N. CHATTERJEA*, S. C. SHAW, Y. PRASAD and R. P. SINGH

Chemistry Department, Patna University, Patna-800 005

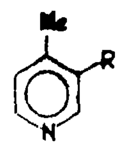
The Hey-Elks route to arylated pyridines has been utilised in the synthesis of 3-azafluorenes. The pyrido-coumarin (23) and the related chromene (24) have been synthesised.

SINCE the first synthesis of 3-azafluorene and its derivatives[1,2] from this laboratory, a number of papers[3-5] have appeared describing researches in this area. The development involved synthesis from appropriate pyridine derivatives. The pyrido-coumarin (**23**) was not known and as its facile transformation into the related chromenes could be predicted, a better route to 3-azafluorene group was sought. It transpired that a short synthesis of 3-aryl-4-methylpyridines may be effected by using free-radical substitution in pyridine system following classical researches of Hey *et al.*[6] and a successful outcome of this approach is described herein.

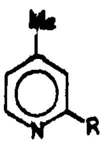
Free aryl radicals could be generated by the decomposition of relevant triazens. Thus, 1-(2'-naphthyl)-3,3'-dimethyltriazen (**1**) on reaction with 4-picoline at 100° in presence of hydrogen chloride gave a mixture of 3- and 2-(2'-naphthyl)-4-methylpyridine (**6** and **11**) in the ratio of 2 : 3. Their separation was conveniently effected by fractional crystallisation of the picrates[6,7]. The triazen (**2**) on similar reaction wtih 4-picoline afforded only one product (**12**).



1 R = 2'-$C_{10}H_7$
2 R = 1'-$C_{10}H_7$
3 R = $C_6H_4.CH_3(m)$
4 R = $C_6H_4.OCH_3(m)$
5 R = $C_6H_4.OCH_3(o)$



6 R = 2'-$C_{10}H_7$
7 R = 1'-$C_{10}H_7$
8 R = $C_6H_4.CH_3(m)$
9 R = $C_6H_4.OCH_3(m)$
10 R = $C_6H_4.OCH_3(o)$

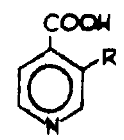


11 R = 2'-$C_{10}H_7$
12 R = 1'-$C_{10}H_7$
13 R = $C_6H_4.CH_3(m)$
14 R = $C_6H_4.OCH_3(m)$
15 R = $C_6H_4.OCH_3(o)$

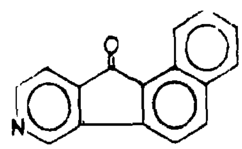
The formation of a single isomer may be explained by the strong steric repulsion of the methyl group and *peri*-hydrogen atom when the 1'-naphthyl radical attacks the 3-position. In the preparation of **10**, the presence of the isomer **15** could not be detected. Here too, the *ortho*-methoxyl group of the attacking radical was responsible for the formation of the product. Excepting these, all other triazens (**3-4**) have produced pairs of isomers (**8-14**). In all of these cases, 2-aryl-4-picolines are formed in greater amount for steric reasons.

The oxidation of aryl-4-picolines by potassium permanganate could not be successfully carried out. Use of selenium dioxide in xylene under the conditions laid down by Marcot and Pollard[8] also proved abortive even when the reaction was carried out under forcing conditions. Success was eventually obtained by employing the same reagent using the recipe of Jackson *et al.*[9] with a slight modification when 54-67% of the acids (**16-19**) were obtained. Similarly, the 2-arylated pyridines (**11-15**) were smoothly oxidised. Some of these acids were decarboxylated (using copper-bronze) and the corresponding aryl pyridines isolated which were characterised (see experimental).

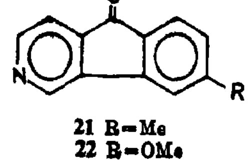
The acid chloride derived from **16** was smoothly cyclised by aluminium chloride in nitrobenzene to give the azafluorenone (**20**) as an orange solid. Similarly, **21** and **22** were obtained ; these were not accompanied by isomeric products. Each of the azafluorenones was derivatised and their uv and ir spectra studied.



16 R = 2'-$C_{10}H_7$
17 R = $C_6H_4.CH_3(m)$
18 R = $C_6H_4.OCH_3(m)$
19 R = $C_6H_4.OCH_3(o)$

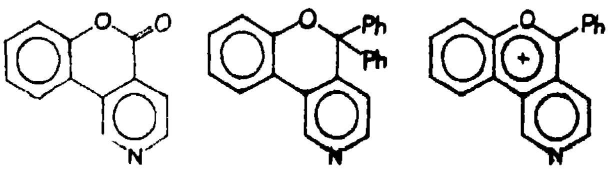


20



21 R = Me
22 R = OMe

3-(2'-Methoxyphenyl)pyridine-4-carboxylic acid on demethylation (hydrobromic acid/acetic acid) gave a quantitative yield of the coumarin (**23**) ν_{max} 1725 cm^{-1} (CO). When treated with phenylmagnesium bromide **23** gave the diphenylchromene derivative (**24**).



23 **24** **25** (*m/z* 258)

The structure is supported by ir spectrum (absence of C=O) and by mass spectrum which showed M^+ 335 with a base peak at *m/z* 258 which undoubtedly corresponds to the pyrylium ion (**25**).

Experimental

All melting points are uncorrected. The infrared spectra were recorded on Perkin-Elmer 237 and 577 spectrophotometer.

1-(2'-Naphthyl)-3,3-dimethyltriazen (**1**) : A suspension of 2-naphthylamine (5.0 g) in concentrated hydrochloric acid (20 ml) was cooled and treated with cold aqueous sodium nitrite solution (2.6 g in 6.5 ml) dropwise and the temperature maintained below 4°. The resulting 2-naphthyldiazonium chloride solution was added dropwise to a mixture of dimethylamine solution (14 ml, 40%) and sodium carbonate solution (150 ml, 30%) in water with stirring during 2 h. A dark red solid separated which was filtered, dried and crystallised from petroleum ether (b.p. 60-80°) as shining colourless needles, m.p. 58° (lit.[9] 57-58°). The other substituted triazens were also prepared in the similar manner. 1-(1'-Naphthyl)-3,3-dimethyltriazen (**2**) was obtained as a viscous reddish oil, b.p. 120°/0.8 mm (lit.[10,11] 127°/0.6 mm, m.p. 41°) ; 1-(*m*-tolyl)-3,3-dimethyltriazen (**3**) as a liquid, b.p. 122°/22 mm (lit.[11] 79°/35 mm) ; 1-(*m*-methoxyphenyl)-3,3-dimethyltriazen (**4**) as a liquid, b.p. 139°/7 mm (lit.[11] 105/0.6 mm) ; 1-(*o*-methoxyphenyl)-3,3-dimethyltriazen (**5**) as a liquid, b.p. 159-160°/15 mm (lit.[12] 123-24°/8 mm).

3-(2'-Naphthyl)-4-methylpyridine (**6**) *and 2-(2'-naphthyl)-4-methylpyridine* (**11**) : 1-(2'-Naphthyl)-3,3-dimethyltriazen (4.0 g) was dissolved in dry 4-picoline (40 ml). The reaction mixture was saturated with hydrogen chloride at 100°. The solidified mass was left overnight at room temperature. The solid mass was made strongly alkaline with sodium hydroxide solution (50%). The mixture was extracted with benzene and evaporation of the dried extract (KOH) gave an oil which was distilled at 160-185°/0.6 mm. Tlc showed two distinct spots corresponding to **6** and **11**. For the separation of these a saturated solution of picric acid (1.6 g) in alcohol was added to the alcoholic solution of the mixture. The mixture was boiled, left for crystallisation. The mixture of picrates was filtered and on repeated fractional crystallisation furnished two picrates (i) picrate of **6**, m.p. 182 (Found : C, 58.59 ; H, 4.39. $C_{22}H_{16}N_4O_7$ requires C, 58.93 ; H, 3.60%), (ii) picrate of **11**, m.p. 212° (Found : C, 58.49 ; H, 3.89. $C_{22}H_{16}N_4O_7$ requires C, 58.92 ; H, 3.60%). The picrate of **6** was mixed with concentrated ammonia (50 ml) and the mixture was left overnight. The reaction mixture was heated for 10 min on a water bath and then cooled. On extraction with benzene and evaporation of the dried extract (KOH) a liquid was obtained which distilled at 165°/0.6 mm to furnish **6** (Found : C, 87.30 ; H, 6.45. $C_{16}H_{13}N$ requires C, 87.64 ; H, 5.98%). Similarly, the picrate of **11** yielded **11** as a viscous oil which solidified on keeping. It crystallised from petroleum ether (b.p. 60-80°) in colourless prisms (0.52 g), m.p. 59-60° (Found : C, 87.25 ; H, 6.3. $C_{16}H_{13}N$ requires C, 87.64 ; H, 5.98%). Similarly, **7-11** and **12-15** were separated by way of their picrates (Table 1).

3-(2'-Naphthyl)pyridine-4-carboxylic acid (**16**) : A mixture of 3-(2'-naphthyl)-4-methylpyridine (0.5 g, 1 mol) and selenium dioxide (0.5 g, 2 mol) in dry pyridine (10 ml) was heated at 105° under anhydrous condition for 10 h and then left at room temperature. The separated selenium was removed by filtration and the filtrate was concentrated under reduced pressure to remove pyridine. The residue was dissolved in saturated sodium bicarbonate solution and filtered. The filtrate on acidification (HCl) yielded 3-(2'-naphthyl)pyridine-4-carboxylic

TABLE 1

Compd no.	M.p. °C	Molecular formula	Analysis % : Found/(Calcd). C	H	Picrate M.p. °C	Picrate Molecular formula	Picrate Analysis % : Found/(Calcd). C	H	N
12	98	$C_{16}H_{13}N$	87.20 (87.64)	6.20 (5.98)	221	$C_{22}H_{16}N_4O_7$	58.72 (58.93)	4.80 (4.39)	12.20 (12.50)
8	50	$C_{13}H_{13}N$	84.91 (85.20)	7.31 (7.15)	152	$C_{19}H_{16}N_4O_7$	55.23 (55.34)	4.13 (3.91)	13.88 (13.59)
13	77	$C_{13}H_{13}N$	84.98 (85.20)	7.27 (7.15)	182	$C_{19}H_{16}N_4O_7$	55.10 (55.34)	4.20 (3.91)	13.25 (13.59)
9	Yellow oil	$C_{13}H_{13}NO$	78.15 (78.36)	6.61 (6.58)	140	$C_{19}H_{16}N_4O_8$	52.75 (53.27)	3.83 (3.77)	12.87 (13.08)
14	Yellow oil	$C_{13}H_{13}NO$	78.20 (78.36)	6.59 (6.58)	165	$C_{19}H_{16}N_4O_8$	52.95 (53.27)	3.98 (3.77)	12.85 (13.08)
10	Yellow oil	$C_{13}H_{13}NO$	78.18 (78.36)	6.41 (6.58)	183	$C_{19}H_{16}N_4O_8$	52.95 (53.27)	5.06 (3.77)	13.08 (13.08)

acid (3.38 g) (**16**). It was crystallised from ethanol in needles, m.p. 284-85° (Found : C, 76.82 ; H, 4.67. $C_{16}H_{11}NO_2$ requires C, 77.09 ; H, 4.45%), ν_{max} 1715 cm^{-1} (COOH). Similarly prepared, 3-(*m*-tolyl)pyridine-4-carboxylic acid (**17**) was obtained as shining colourless crystals, m.p. 232° (Found : C, 73.16 ; H, 5.35 . $C_{13}H_{11}NO_2$ requires C, 73.22 ; H, 5.20%), ν_{max} 1720 cm^{-1} (COOH) ; 3-(*m*-methoxyphenyl)pyridine-4-carboxylic acid (**18**) as colourless shining crystals, m.p. 180° (Found : C, 67.85 ; H, 5.1 . $C_{13}H_{11}NO_3$ requires C, 68.11 ; H, 4.85%), ν_{max} 1720 cm^{-1} (COOH) ; 3-(*o*-methoxyphenyl)pyridine-4-carboxylic acid (**19**) in prisms, m.p. 238° (Found : C, 67.82 ; H, 5.20 . $C_{13}H_{11}NO_3$ requires C, 68.11 ; H, 4.85%), ν_{max} 1700 cm^{-1} (COOH).

By adopting a similar procedure 2-(2'-naphthyl)-pyridine 4-carboxylic acid was obtained as needles, m.p. 287° (Found : C, 76.79 ; H, 4.50 . $C_{16}H_{11}NO_2$ requires C, 77.09 ; H, 4.45%), ν_{max} 1715 cm^{-1} (COOH) ; 2-(1'-naphthyl)pyridine-4-carboxylic acid as colourless needles, m.p. 256° (Found : C, 77.0 ; H, 4.50 . $C_{16}H_{11}NO_2$ requires C, 77.09 ; H, 4.45%), ν_{max} 1715 cm^{-1} (COOH) ; 2-(*m*-tolyl)pyridine-4-carboxylic acid as shining colourless crystals, m.p. 241° (Found : C, 73.10 ; H, 5.29 . $C_{13}H_{11}NO_2$ requires C, 73.22 ; H, 5.20%), ν_{max} 1720 cm^{-1} (COOH); 2-(*m*-methoxyphenyl)pyridine-4-carboxylic acid as colourless crystals, m.p. 203° (Found : C, 67.80 ; H, 5.20 . $C_{13}H_{11}NO_3$ requires C, 68.11 ; H, 4.85%), ν_{max} 1720 cm^{-1} (COOH).

3-(2'-Naphthyl)pyridine : A mixture of 3-(2'-naphthyl)pyridine-4-carboxylic acid (0.04 g) and copper-bronze (0.06 g) was heated gently till the evolution of gas ceased. The mass was extracted with benzene and chromatographed over alumina. 3-(2'-Naphthyl)pyridine was obtained as crystals, m.p. 101° (lit.[13] 102-103°). The picrate was crystallised from ethanol in yellow needles, m.p. 202° (lit.[13] 200°). Similarly prepared, 3-*m*-tolyl)pyridine was obtained as an yellow oil, the picrate separated as yellow prisms, m.p. 187° (Found : C, 84.96 ; H, 6.65 . $C_{12}H_{11}N$ requires C, 85.17 ; H, 6.55%) ; 3-(*o*-methoxyphenyl)pyridine as yellow oil, the picrate separated as yellow needles, m.p. 180° (lit.[14] 182°).

By applying the same procedure 2-(2'-naphthyl)-pyridine was obtained as colourless crystals, m.p. 72° (lit.[15] 71-72°), the picrate separated as yellow needles, m.p. 178-180° (lit.[15] 175-175.5°) ; 2-(1'-naphthyl)pyridine as yellow oil, the picrate separated as yellow needles, m.p. 197° (lit.[16,17] 199.5°) ; 2-(*m*-tolyl)pyridine as yellow oil, the picrate separated as yellow prisms, m.p. 183° (lit.[18] 183.5°) ; 2-(*m*-methoxyphenyl)pyridine as yellow oil, the picrate as yellow needles, m.p. 154° (lit.[19] 154-155°).

7,8-Benzo-3-azafluorenone (**20**) *:* The acid chloride prepared from 3-(2'-naphthyl)pyridine-4-carboxylic acid (**16**) (0.2 g) was dissolved in dry nitrobenzene and powdered anhydrous aluminium chloride (0.3 g) was added with occasional shaking. The colour changed to orange red. The reaction mixture was left overnight at room temperature and steam distilled. 7,8-Benzo-3-azafluorenone (**20**) was separated as orange-red solid which crystallised from benzene in orange-red small needles (0.13 g, 70%), m.p. 195° (Found : C, 82.88 ; H, 4.2 . $C_{16}H_9NO$ requires C, 83.10 ; H, 3.92%), ν_{max} 1700 cm^{-1} (CO) ; λ_{max} 246, 292, 385 nm, log ϵ 4.54, 4.32, 3.66. Similarly, 6-methyl-3-azafluorenone (**21**) separated as yellow shining crystals (76%), m.p. 105° (Found : C, 79.88 ; H, 4.78 . $C_{13}H_9NO$ requires C, 79.98 ; H, 4.65%), ν_{max} 1710 cm^{-1} (CO) ; λ_{max} 258, 328 nm ; log ϵ 4.44, 3.54 ; 6-methoxy-3-azafluorenone (**22**) as yellow shining crystals (73%), m.p. 185° (Found : C, 73.80 ; H, 4.51 . $C_{13}H_9NO_2$ requires C, 73.92 ; H, 4.30%), ν_{max} 1700 cm^{-1} (CO) ; λ_{max} 277, 245 nm ; log ϵ 4.32, 3.70.

*Pyrido[4,3-*c*] coumarin* (**23**) *:* A mixture of 3-(*o*-methoxyphenyl)pyridine-4-carboxylic acid (**19**) (0.2 g) and hydrobromic acid (0.3 ml, 48%) in glacial acetic acid (6 ml) was refluxed at 130° for 6 h. Acetic acid was removed under reduced pressure and diluted with water. Pyrido[4,3-*c*]coumarin which separated was crystallised from benzene in needles (0.7 g), m.p. 186°. The compound was insoluble in cold sodium bicarbonate solution (Found : C, 73.0 ; H, 4.1 . $C_{12}H_7NO_2$ requires C, 73.09 ; H, 3.85%), ν_{max} 1725 cm^{-1} (lactone ring). The picrate separated in yellow needles, m.p. 230° (Found : C, 50.61 ; H, 2.47 . $C_{18}H_{10}N_4O_9$ requires C, 50.70 ; H, 2.35%).

2,2-Diphenylbenzo[b]*pyrido[4,3*-d] *-1,2-pyran* (**24**) *:* Pyrido[4,3-*c*]coumarin (0.05 g, 1.0 mol) in dry benzene was added to the ethereal solution of phenylmagnesium bromide (0.116 g, 2.5 mol) (prepared from magnesium 0.016 g and bromobenzene 0.1 g). The mixture was refluxed for 4 h and left overnight. On working up in the usual manner 2,2-diphenylbenzo[b]pyrido[4,3-*d*]-1,2-pyran (**24**) separated as white crystals which was crystallised from benzene-petroleum ether as shining needles, m.p. 198° (Found : C, 85.83 ; H, 5.30 . $C_{24}H_{17}NO$ requires C, 85.94 ; H, 5.11%) ; M^+ (*m*/*z*) 335 (base peak 258).

References

1. J. N. Chatterjea and K. Prasad, *J. Indian Chem. Soc.*, 1960, **37**, 357.
2. J. N. Chatterjea and K. Prasad, *Chem. Ber.*, 1960, **93**, 1740.
3. H. Pines, S. V. Kannan and W. M. Stalick, *J. Org. Chem.*, 1971, **36**, 2308.
4. A. Ebnorther, J. M. Bastian and E. Rissi, *Chem. Abstr.*, 1972, **76**, 153613 ; A. Ebnorther, J. M. Bastian and F. Gadient, *Chem. Abstr.*, 1973, **78**, 4141.
5. N. S. Prostakov, V. O. Fedorov and A. T. Soldatenkov, *Khim. Geterotsikl. Soedin.*, 1979, **8**, 1098 (*Chem. Abstr.*, 1979, **91**, 193141).
6. J. Elks and D. H. Hey, *J. Chem. Soc.*, 1943, 443.
7. J. W. Haworth, J. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 1940, 349.
8. B. Marcot and R. Pollard, *C. R. Hebd. Seances Acad. Sci.*, 1959, **248**, 252.
9. A. Jackson, N. D. V. Wilson, A. J. Gaskell and J. A. Joule, *J. Chem. Soc.* (C), 1969, 2745.

10. C. S. RONDESTVEDT, JR. and S. J. DAVIS, *J. Org. Chem.*, 1957, **22**, 202.
11. Z. VLADIMIR, D. JIRI, N. JOSEF and M. MIROSTOV, *Chem. Abstr.*, 1969, **71**, 70216.
12. W. J. ADAMS and D. H. HEY, *J. Chem. Soc.*, 1951, 1526.
13. W. L. BENCZE and L. I. BARSKY, *J. Med. Pharm. Chem.*, 1962, **5**, 1298.
14. J. W. HAWORTH, I. M. HEILBRON and D. H. HEY, *J. Chem. Soc.*, 1940, 359.
15. N. A. NELSON, L. A. PAQUETTE, *J. Org. Chem.*, 1962, **27**, 964.
16. C. K. BRADSHER and L. E. BEAVERS, *J. Am. Chem. Soc.*, 1956, **78**, 2459.
17. E. E. GLOVER and G. JONES, *J. Chem. Soc.*, 1959, 1686.
18. C. W. N. CUMPER, R. F. A. GINMAN and A. I. VOGEL, *J. Chem. Soc.*, 1962, 4526.
19. J. W. HAWORTH, J. M. HEILBRON and D. H. HEY, *J. Chem. Soc.*, 1940, 3C'

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1032-1033

[13]C Nmr Spectra of Acutangulic and Tangulic Acids from *Barringtonia acutangula* Gaertn.

K. DHAVEJI, G. K. A. S. S. NARAYAN, D. S. RAO and L. RAMACHANDRA ROW*

Department of Chemistry, Andhra University, Waltair-530 003

[13]C nmr spectra of acutangulic and tangulic acids are now presented in support of the structures 1 and 2 proposed earlier. The effect of the 18β-hydroxyl on the C12-13 olefinic bond is discussed.

FROM the leaves of *Barringtonia acutangula* Gaertn., two rare triterpene carboxylic acids, acutangulic and tangulic acids (1 and 2) were isolated in these laboratories[1]. The former was shown to be 2α, 3β,18β-trihydroxyolean-12-en-28-oic acid (1), and the latter 2α,3β,18β-trihydroxyolean-12-en-23,28-dioic acid (2). These assignments were supported by [1]H nmr, mass spectra and chemical evidence. The configuration of the 18-hydroxyl was suggested to be β-equatorial as both acids failed to give a triacetate or a lactone even under forced conditions. To confirm the above structures, [13]C nmr spectra of their diacetates were secured and results presented here.

Experimental

The leaves (2 kg) of *Barringtonia acutangula* Gaertn. were successively extracted with hexane, ethyl acetate and methanol. Separation of the individual components from the above extracts was achieved by fractional crystallisation followed by column chromatography on silica gel G as reported earlier[1]. γ-Sitosterol, β-sitosterol, β-D(+)-glucopyranoside, barrigtonic acid, β-amyrin, oleanolic acid, tangulic acid and acutangulic acid were identified in the usual manner (m.m.p., ir, and [1]H nmr).

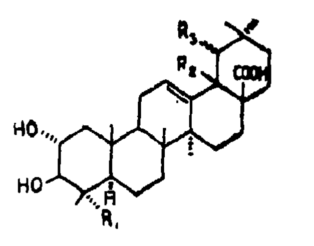
The diacetates of acutangulic and tangulic acids were prepared by the action of Ac_2O/Py at 100°. The [13]C nmr spectra of these diacetates were recorded on Varian spectrometer at 67.89 MHz in d_6-DMSO with TMS as internal standard and the assignments are presented in Table 1.

TABLE 1—[13]C NMR SPECTRA

	Methyl maslinate[3] (3) $CDCl_3$	Acutangulic acid (1) diacetate d_6-DMSO	Tangulic acid (2) diacetate d_6-DMSO
C-1	46.4	46.94	46.97
C-2	66.5	71.77	71.74
C-3	78.9	79.95	78.25
C-4	39.1	38.75	54.59
C-5	55.3	54.13	49.01
C-6	18.3	17.92	19.56
C-7	32.6	32.40	32.55
C-8	39.1	37.95	38.10
C-9	47.5	46.41	46.18
C-10	38.3	38.94	38.95
C-11	23.1	23.87	23.87
C-12	122.0	126.80	126.50
C-13	143.6	138.73	138.69
C-14	41.7	44.53	43.96
C-15	27.6	27.50	25.92
C-16	23.5	23.16	23.25
C-17	46.6	54.07	54.95
C-18	41.3	69.19	69.13
C-19	45.8	53.16	53.29
C-20	30.7	28.09	28.09
C-21	33.8	32.40	32.55
C-22	32.8	28.08	28.09
C-23	28.6	27.96	174.47
C-24	16.8	17.33	25.27
C-25	16.8	16.56	16.46
C-26	16.8	16.15	16.15
C-27	26.0	26.25	26.35
C-28	178.0	178.75	178.75
C-29	33.1	37.14	37.11
C-30	23.5	23.16	23.78
CH_3COO	—	20.16, 169.92	20.58, 170.23
CH_3COO	—	20.65, 169.67	20.68, 169.51

Results and Discussion

Like maslinic acid (3), the acutangulic and tangulic acids (1 and 2) are 2α,3β-diols and their [13]C nmr spectra resemble very closely. Introduction of an equatorial hydroxyl at C-2 has a marked downfield shift of about δ 8.2 on C-1 in 1 and 2, (C-1, δ 46.94, 46.97) as in methyl maslinate (C-1, δ 46.4), compared to that of methyl oleanolate[3] (C-1, δ 38.2). Similar correspondance of the C-4 and C-10 shifts in 1 and 2 are also observed with those of methyl maslinate (3).



1 R_1=CH_3, R_2=β-OH, R_3=H
2 R_1=COOH, R_2=β-OH, R_3=H
3 R_1=CH_3, R_2=R_3=H
4 R_1=CH_3, R_2=H, R_3=α-OH.

TABLE 2

	Methyl oleanolate	Methyl maslinate[5]	Arjunic acid[4]	3,19-diol 28-COOMe[7]	Acutangulic acid diacetate	Tangulic acid diacetate
	$CDCl_3$	$CDCl_3$	DMSO	$CDCl_3$	DMSO	DMSO
C-12	121.5	122.0	123.4	126.9	126.8	126.52
C-13	144.9	143.6	144.9	138.7	138.73	138.69

In tangulic acid (2) diacetate*, replacement of 23α-equatorial methyl by a carboxyl caused a marked downfield shift of 15.84 ppm in C-4 resonance (δ 54.59) compared to δ 38.75 of C-4 in the acutangulic acid diacetate. This carboxyl has the expected γ-effect, *i.e.* δ+1.5 on C-3 and +5.12 ppm on C-5, comparable to those recorded for pimaradiene and pimaric acid[5,6].

The olefinic carbons, C-12 and C-13, appeared at δ 126.80 and 138.73 for **1** and at 126.52 and 138.69 for **2**, significantly different from those of methyl maslinate or methyl oleanolate (Table 2) in which the D/E ring-junction is known to be *cis*. It is clear that the 18β-equatorial hydroxyl of **1** and **2** caused a prominant downfield shift of δ 4.8 of C-12 but an equal and opposite effect is experienced by C-13.

The effect of hydroxyl on 12-13 olefinic bond in oleanenes and ursenes was studied by Lewis *et al.*[7] with the help of ¹³C nmr. He records that the 19-hydroxyl in oleanenes, if equatorial, exerts the same influence as the 19β-methyl in ursenes (Table 2) and, therefore, concludes that the chemical shift change is due to the steric influence of 19β-hydroxyl. The 19α-hydroxyl of oleanenes has only a minor effect.

In the acutangulic acid and tangulic acid, the effect of 18β-hydroxyl is very similar to that of 19β-hydroxyl. This may not be taken to be entirely due to the steric influence in view of the polar character of the hydroxyl, unlike the 19β-methyl of the ursenes. On a close examination of the molecular models (constructed out of dreiding models) the 18β-hydroxyl is equidistant between C-12 and C-13 approximately within 2.1 Å. In another conformation, this hydroxyl approaches C-12 within 1.9 Å and C-13 within 2.18 Å approximately. This is quite comparable to that of 19β-hydroxyl which approaches C-12 or C-13 within approximately 2.1 Å and 2.5 Å, respectively. Thus, the 18β- and 19β-hydroxyls are quite close to the π electron system of 12-13 bond (D/E *cis*) and, therefore, possess similar effect on C-12 and C-13, the former being deshielded by about δ 4.8 to 5.3 and the latter shielded by about δ 4.9 to 6.2 (*cf.* Ref. 8).

It is significant to record in this connection that in arjunic acid (4)[4], the 19α-axial hydroxyl does not have any recognisable effect on C-12 or C-13. If D/E ring is *trans*, the 18-hydroxyl assumes α-axial configuration and is far removed from C-12 or C-13 and leaves them unaffected, thus confirming the 18β-hydroxyl in acutangulic and tangulic acids (**1** and **2**).

The *cis* D/E junction is further supported by the C-17 resonances (δ 54.07 in **1** and 54.95 in **2**) around 8 ppm downfield compared to that of methyl maslinate (δ 46.6). The remaining assignments are entirely in agreement with the structures proposed for these acids (**1** and **2**).

* Barrigenic acid[a] from the fruits is the 19β-hydroxy isomer and barrinic acid[b] from the branch wood is 19α-hydroxy isomer. Both differ extensively from **2**.

[a]A. K. Barua, P. Chakrabarthi, A. S. Dutta Gupta, S. K. Paul, A. S. Basak, S. K. Mukharjee and K. Basu, *Phytochemistry*, 1976, **15**, 1780. [b]A. K. Barua, S. K. Paul and S. P. Dutta, *J. Indian Chem. Soc.*, 1972, **49**, 519.

Acknowledgement

One of the authors (K.D.) thanks the U.G.C., New Delhi, for F.I.P. Fellowship during this work. The authors thank Prof. G. S. R. Subba Rao, Indian Institute of Sciences, Bangalore for ¹³C nmr spectra.

References

1. A. S. R. Anjaneyulu, C. S. P. Sastry, G. K. A. S. S. Narayan and L. R. Row, *J. Indian Chem. Soc.*, 1978, **55**, 1169.
2. S. Sao, Y. Tomita and K. Tori, *Tetrahedron. Lett.*, 1976, 7.
3. J. D. Roberts, F. J. Weigert, J. I. Kroschwitz and R. J. Reich, *J. Am. Chem. Soc.*, 1970, **92**, 1338.
4. A. S. R. Anjaneyulu and A. V. Rama Prasad, *Phytochemistry*, 1982, **21**, 2057.
5. M. Gordon, S. H. Grover and J. B. Strothers, *Can. J. Chem.*, 1973, **51**, 2092.
6. E. Wenkert and B. L. Buckwalter, *J. Am. Chem. Soc.*, 1972, **94**, 4367.
7. D. M. Doddrell, P. M. Khong and K. G. Lewis, *Tetrahedron Lett.*, 1974, 2381.
8. H. E. Gottlieb and I. Kirson, *Org. Magn. Reson.*, 1981, **16**, 20.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1034-1037

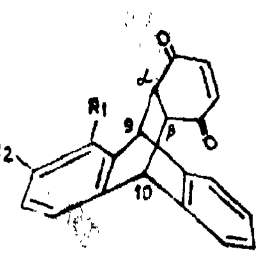
Stereochemical Assignment by Nmr Spectroscopy. Diels-Alder Adducts of *p*-Benzoquinone with Cyclic Dienes

SUBODH MAHANTI, HAWALDAR MAURYA and SHIVA M. VERMA*

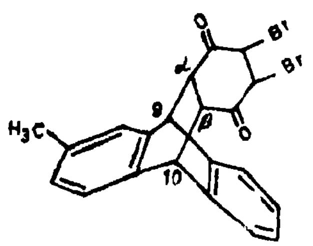
Department of Chemistry, Banaras Hindu University, Varanasi-221 005

Nmr spectroscopy has been employed to demonstrate the stereochemistry of Diels-Alder adducts of *p*-benzoquinone with substituted anthracenes by transforming the mono adducts into bis adducts. Restricted rotation about N-CO bonds and a preferred *trans* arrangement has been proposed for the C(1)-diacetamido group in 1-diacetamidoanthracene-*p*-benzoquinone adduct. It has been observed that the spectral pattern may not be diagnostic in configurational assignment of bis adducts of *p*-benzoquinone with similar dienes but may provide valuable information about the adducts with dissimilar dienes.

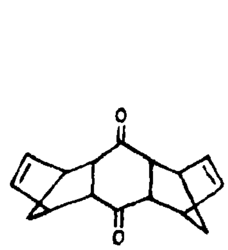
DIELS-ALDER reaction of *p*-benzoquinone with 1- and 2-substituted anthracenes may lead to configurational isomers (*syn* and *anti*) depending on the steric and electronic effects of the substituents. Spectral data of the adducts particularly when only one isomer is formed may not provide convincing evidence regarding the geometry of the molecule. Stereochemistry of the Diels-Alder adducts of maleic anhydride with cyclic dienes has been successfully demonstrated[1] with the help of conformational analysis about N-N and N-C bonds through their *N*-imide derivatives. However, this technique could not be applied in case of *p*-benzoquinone-anthracene adducts. Nmr spectroscopy may not be very helpful in configurational assignments of bis adducts of *p*-benzoquinone with similar dienes due to the symmetrical nature of the molecules. In this communication we report the introduction of a dissimilar diene to *p*-benzoquinone mono adducts and its potentiality as a probe in the configurational assignments. For this purpose, compounds (**1-10**) were prepared and were characterized by elemental analyses and spectral data (Tables 1-3).



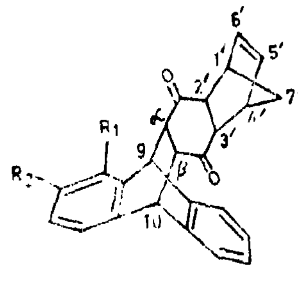
1 R_1=NAc_2, R_2=H
2 R_1=H, R_2=NAc_2
3 R_1=H, R_2=CH_3
4 R_1=R_2=H



5



6



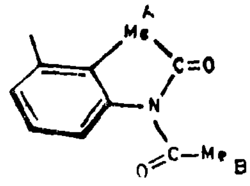
7 R_1=NAc_2, R_2=H
8 R_1=H, R_2=NAc_2
9 R_1=H, R_2=CH_3
10 R_1=R_2=H

Results and Discussion

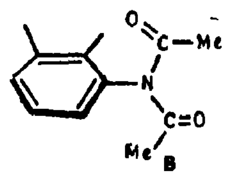
Pmr spectrum of Diels-Alder (DA) adduct of 1-diacetamidoanthracene and *p*-benzoquinone (**1**) exhibits two singlets at δ 1.68 and 2.56 each of 3H intensity for the two acetyls, along with other resonances (Table 1). The position of the acetyl resonances and their internal separation ($\Delta\delta = 1$ ppm) in compound **1** are very much similar to that of the *anti* isomer of 1-diacetamidoanthracene-maleic anhydride adduct[2], suggesting for the *anti* configuration of the adduct **1**. In case of *syn* configuration one of the olefinic protons would have been influenced by *N*-diacetamido group but a sharp singlet (2H) at δ 6.40 further suggests *anti* configuration.

The conformational analysis about N-CO bonds of 1-*N*-diacetamido group in **1** has proved to be interesting. In 1-diacetamidoanthracene and related system[3] the appearance of C(1)-N$(COCH_3)_2$ as a singlet provides evidence for the magnetic equivalence of the two acetyls. Hindered rotation[3] about C(1)-N bond is evident in such compounds due to the interaction of C(9) hydrogen with the C(1) substituents and free rotation about N-CO

bonds may render the acetyls to be magnetically equivalent. In compound **1** the appearence of two acetyl resonances at δ 1.78 and 2.78 must emerge from a preferred conformation about N – CO bonds with *trans* arrangement[4] like **11** or **12**. The shielding parameter (0.25 ppm) of C-9 proton with respect to C-10 proton could be exploited to distinguish between the two conformers **11** and **12**. Molecular models show that in **12**, C-9 proton falls in the shielding zone of C=O and the acetylmethyl (MeB) would undergo a diamagnetic shift since it lies towards the benzo ring. Conformer **12** thus accounts for both the shielding of C-9 proton and for the internal chemical shift of the two acetylmethyls.



11

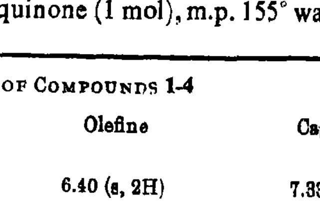


12

^{13}C nmr spectrum of compound **1** has further provided additional evidence in support of the preferred *trans* arrangement of 1-*N*-diacetamido group. The spectrum exhibits resonances at δ 26.13 and 27.11 (acetylmethyl carbons), 43.62 and 47.62 (C-9 and C-10), 48.20 and 48.70 (C-α and C-β), 173.23 and 173.19 (amide carbonyl carbons) and 194.60 and 195.03 for the carbonyl carbons of cyclohexanedione moiety. ^{13}C nmr spectrum of *p*-benzoquinone-anthracene adduct (**4**) exhibits resonances at δ 48.92 (C-9 and C-10), 49.12 (C-α and C-β) and 194.03 (carbonyl carbons). A considerable shielding (5 ppm) of C-9 resonance in **1** would not be expected through bond interactions but may be due to crowding effect or 'field effect' (through space effect) of the substituent[5]. The shielding parameter (~ 1 ppm) between two methyl carbons in **1** suggests that the shielding is not caused by methyl group[6] in **11** but likely through space effect of the carbonyl group in **12**. The appearance of the two amide carbonyl carbons at δ 172.03 and 173.19 supports the proposed preferred conformation and restricted rotation about N – CO bonds.

2-Diacetamidoanthracene and *p*-benzoquinone gave only one DA adduct. The appearance of the acetyl resonances at the normal position as a singlet in the pmr spectrum of the adduct **2** (Table 1) indicate free rotation about N – CO bonds. It is not evident from the spectral data whether the adduct is *syn* or *anti*, though on theoretical grounds one would expect the adduct to be *anti*. ^{13}C nmr spectrum of compound **2** exhibits resonances at δ 26.75 (acetylmethyl carbons), 48.98 and 48.67 (C-9 and C-10), 49.01 (C-α and C-β), 173.25 (amide carbonyl carbons) and 194.72 (carbonyl carbons of the cyclohexanedione moiety). ^{13}C spectrum **2** thus indicates free rotation about N – CO bonds of the diacetamido group but does not provide any convincing clue about its configuration.

2-Methylanthracene with *p*-benzoquinone gave an adduct (**3**), m.p. 204-5°. The spectral pattern (Table 1) does not provide any definite evidence about its geometry but the dibromo product (**5**) exhibits a singlet (3H) at δ 2.26 for (CH_3), a broad singlet (2H) at 3.60 (C-α and C-β protons) and AB quartet centred at 4.4 (CHBr methine protons), two broad singlets at 4.95 and 5.03 (each 1H) for C-9 and C-10 protons alongwith a multiplet (7H) at 7.3 for the cage-aromatic protons. Spectral studies of some brominated products have shown[7] CHBr methine protons to be magnetically non-equivalent in *trans* addition of bromine to the olefinic bond. Thus an AB quartet in **5** suggests *trans* addition and the structure could be proposed as **14** where cyclohexanedione ring has somewhat a chair type conformation with the bromine atoms in *trans* diaxial orientation. The strong absorption[8] at 1720 cm^{-1} in the ir spectrum for carbonyl stretching supports the diaxial nature of the bromine atoms. Moreover, from the magnetic non-equivalence of C-9 and C-10 protons in **5**, it could be reasonably proposed that one of the carbonyls may be twisted below to cause deshielding of C-9 proton. The unaffected methyl resonance in **5** suggests *anti* configuration of the adduct.



13

A bis DA adduct (**6**) of cyclopentadiene (2 mol) and *p*-benzoquinone (1 mol), m.p. 155° was obtained[9].

TABLE 1—NMR (60 MHz) SPECTRAL DATA* (δ ppm) OF COMPOUNDS 1-4

Compd. no.	R_1/R_2	α+β	9+10	Olefine	Cage-aromatic
1	1.68 (s, 3H) 2.56 (s, 3H)	3.02 (t, 2H)	4.61 (bs, 1H) 4.85 (bs, 1H)	6.40 (s, 2H)	7.33 (m, 7H)
2	2.18 (s, 6H)	3.20 (t, 2H)	4.97 (bs, 2H)	6.43 (s, 2H)	7.0-7.60 (m, 7H)
3	2.25 (s, 3H)	3.18 (t, 2H)	4.86 (bs, 2H)	6.46 (s, 2H)	7.15 (m, 7H)
4	—	3.15 (t, 2H)	4.92 (t, 2H)	6.33 (s, 2H)	7.30 (m, 8H)

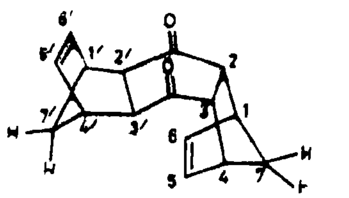
* s=singlet, t=triplet, m=multiplet, bs=broad singlet.

TABLE 2—NMR (60 MHz) SPECTRAL DATA* (δ ppm) OF COMPOUNDS 7-10

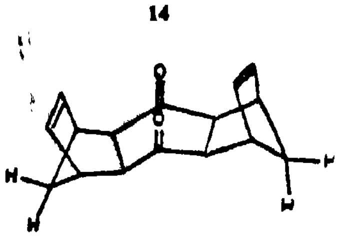
Compd. no.	7′-OH	R′$_1$+R′$_2$	2′+3′	1′+4′	α+β	9+10	5′+6′	Cage-aromatic
7	AB quartet, 2H, J_{AB} 9.1 Hz, A 1.39, B 1.05	1.70 (s, 3H) 2.63 (s, 3H)	2.40 (m, 2H)	2.73 (t, 2H)	3.28 (t, 2H)	4.60 (m, 1H) 4.83 (m, 1H)	6.12 (t, 2H)	7.33 (m, 7H)
8	AB quartet, 2H, J_{AB} 9.0 Hz, A 1.36, B, 1.03	2.24 (s, 6H)	2.41 (m, 2H)	2.83 (m, 2H)	3.27 (m, 2H)	4.76 (bs, 2H)	6.1 (t, 2H)	7.33 (m, 7H)
9	AB quartet, 2H, J_{AB} 9.2 Hz, A 1.31, B 0.98	2.28 (s, 3H)	2.35 (m, 2H)	2.75 (bs, 2H)	3.25 (m, 2H)	4.66 (bs, 2H)	6.1 (t, 2H)	7.16 (m, 7H)
10	AB quartet, 2H, J_{AB} 9.0 Hz, A 1.29, B 0.95	—	2.33 (m, 2H)	2.80 (t, 2H)	3.28 (t, 2H)	4.66 (t, 2H)	6.03 (t, 2H)	7.25 (m, 8H)

* Abbreviation as in Table 1.

Pmr spectrum of 6 exhibits an AB quartet (4H, A δ 1.49, B δ 1.39, J_{AB} 9Hz, 7 and 7′-CH_2), a triplet (4H) at δ 2.90 (1, 4, 1′ and 4′-H), a triplet (4H) at 3.42 (2, 3, 2′ and 3′-H) and a triplet 4(H) at 6.22 (5, 6, 5′ and 6′-H). The spectral pattern of compound 6 depicts a symmetrical geometry of the molecule. It is also evident from molecular models that only *endo-endo* or *exo-exo* configuration would satisfy the condition of symmetry in the molecule. The possibility of *exo-exo* configuration may be excluded by considering the usual pronounced preference for *endo* kinetic control in Diels-Alder reaction[10] and the preference of 14 over the other possible *endo-endo* configuration 15 is expected on steric grounds. The observed spectral pattern would, therefore, favour the *endo-endo* configuration (14) which is in agreement[11] with the earlier proposed structure. It may be pointed out that the spectral pattern of the adduct as such does not rule out the possibility of other symmetrical structures.



14



15

Adduct 1 undergoes further Diels-Alder reaction with cyclopentadiene to form a bis adduct (7) in almost quantitative yield. Considering the *cis* fusion of bicycloheptene nucleus in the bis adduct, the cyclopentadiene may add *syn* or *anti* with respect to the anthracene moiety. On steric grounds the *anti* addition would be the most probable. Diamagnetic shift of 2′, 3′ proton resonances in 7 (Table 3)

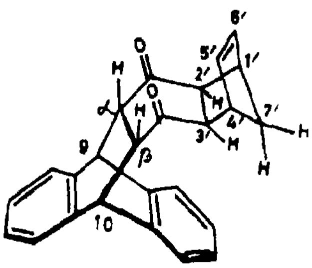
TABLE 3—M p., ELEMENTAL ANALYSES AND CHARACTERISTIC IR PEAKS

Compd. no.	M.p. °C	Analysis % : Found/(Calcd.) C	H	ν^{*}_{max} cm^{-1}
1	193-194	74.60 (74.79)	5.10 (4.97)	1720s, 1680s, 1600w
2	218-219	74.50 (74.79)	5.00 (4.97)	1725s, 1680s, 1600w
3	204-205	83.70 (83.98)	5.80 (5.97)	1680s, 1600w
4	235-236	83.70 (83.90)	5.10 (4.93)	1680s, 1590w, 1580w
5	148-1 0	54.55 (54.81)	3.62 (3.50)	1720s, 1600w, 1380m
6	154-155	80.00 (79.97)	6.48 (6.71)	1680s, 1480w
7	194-195	77.20 (77.14)	5.65 (5.58)	1720s, 1680w, 1660w, 1580w
8	181-182	77.00 (77.14)	5.60 (5.58)	1720s, 1690s, 1660w
9	164-165	85 00 (85.22)	6.10 (6.05)	1700s, 1600w
10	185-186	85.12 (85.20)	5.65 (5.72)	1700s, 1485m

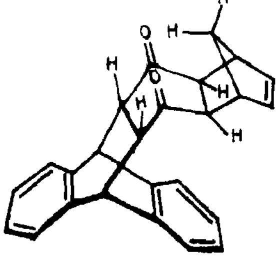
* m = medium, s = strong and w = weak.

further supports the *anti* addition. In case of *syn* addition, 2′, 3′ protons would be on the opposite side of the benzo ring, while in *anti* addition, these protons would fall in the shielding zone of the benzo ring. In *anti* addition and assuming a boat conformation of the central cyclohexanedione ring, two possibilities may arise, the bicycloheptene moiety may be *endo* (16) or *exo* (17). From mechanistic point of view[10] of Diels-Alder reaction the *endo* configuration has been proposed. Further, this is supported by comparatively large chemical shift difference (0.34 ppm) between the two 7′-methylene protons in 7 than in 6, since in *endo* configuration (16) one of the methylene protons would be influenced by the anisotropy effect of benzo ring

of anthracene moiety. So, the configuration of the bis adduct may be proposed as **16**. Magnetic non-equivalence of C-9 and C-10 protons and positions of the two acetyl resonances of **7** are almost same as in **1**, indicating no conformational change in the diacetamido group due to the formation of bis adduct. In case of *syn* configuration the resonance of the acetylmethyl would certainly have been influenced by the formation of bis adduct. The configurational assignment of bis adduct has, therefore, strongly supported the *anti* configuration of the mono adduct (**1**).



16



17

The spectral patterns of the bis adducts (**8-10**) (Table 3) suggest similar configuration as in **1**. Moreover, the formation of bis adduct does not influence the resonances of the substituents in **8** and **9**, thereby, supporting for the *anti* configuration of the mono adducts.

Experimental

All the melting points are uncorrected. Nmr spectra were recorded in $CDCl_3$ with TMS as an internal reference on a Varian A-60D spectrometer at 45°. ^{13}C nmr spectra were recorded on a Perkin-Elmer CFT-20 spectrometer. Ir spectra were recorded in Nujol mull on a Perkin-Elmer 257 spectrophotometer. Melting points, chemical analyses and characteristic ir bands of the compounds are given in Table 3.

Substituted anthracenes : 1-Amino-, 2-amino- and 2-methylanthracenes were prepared by the reduction of their corresponding anthraquinone derivatives by zinc dust and alkali[12]. 1-Aminoanthracene was recrystallised from ethanol, m.p. 126-27° ; 2-aminoanthracene from toluene, m.p. 237-39° ; and 2-methylanthracene from acetone, m.p. 204-6°.

1- and 2-Diacetamidoanthracenes : Compounds were prepared by refluxing the corresponding aminoanthracene with an excess acetic anhydride for about 6 h. 1-Diacetamidoanthracene was recrystallised from ethanol, m.p. 239-41°.

DA adducts of p-*benzoquinone and substituted anthracenes* (**1-4**) : These were obtained[13] by refluxing the corresponding anthracene and its derivatives with *p*-benzoquinone in equimolar proportion in dry xylene for 1 h. The products were recrystallised from benzene.

*2-Methylanthracene-*p*-benzoquinone adduct dibromide* (**5**) : Equimolar amount of bromine in dry chloroform (10 ml) was added dropwise to the stirred solution of the adduct **3** (0.2 g) in chloroform (15 ml) over a period of 2 h. On removal of solvent under reduced pressure a solid material was obtained. It was recrystallised from chloroform.

*Bis-cyclopentadiene-*p*-benzoquinone adduct* (**6**) : It was obtained by stirring freshly distilled cyclopentadiene (0.43 ml) and *p*-benzoquinone (0.52 g) in dry benzene (15 ml) at 5° for about 6 h. After removing the solvent under reduced pressure a white solid material was obtained which on recrystallisation from ethanol gave prismatic crystals.

*Anthracene-*p*-benzoquinone-cyclopentadiene DA adducts* (**7-10**) : These bis adducts were prepared by stirring the corresponding mono adduct with freshly distilled cyclopentadiene in equimolar quantity in dry benzene at 10° for 12 h. After removing the solvent under reduced pressure, the products obtained were recrystallised from ethanol.

Acknowledgement

The authors thank C.S.I.R., New Delhi for the award of two research fellowships (S.M. and H.M.).

References

1. S. M. VERMA and O. S. RAO, *Tetrahedron*, 1974, **30**, 237 ; S. M. VERMA and A. K. SINGH, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 516 ; S. M. VERMA and N. B. SINGH, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 520 ; S. M. VERMA and R. M. SINGH, *Aust. J. Chem.*, 1976, **29**, 1215 ; S. M. VERMA and R. M. SINGH, *J. Org. Chem.*, 1975, **40**, 897 ; M. D. SINGH and S. M. VERMA, *J. Sci. Ind. Res.*, 1980, **82**, 262.
2. S. M. VERMA and M. D. SINGH, *J. Org. Chem.*, 1977, **42**, 3736.
3. S. M. VERMA and N. B. SINGH, *Aust. J. Chem.*, 1976, **29**, 295 ; H. B. PETER, L. D. COLEBROOK, R. A. FRASER and H. G. GILES, *J. Chem. Soc., Chem. Commun.*, 1974, 225 ; L. D. COLEBROOK, H. G. GILES, A. GRANATA and S. ICLI, *Can. J. Chem.*, 1973, **51**, 3635 ; W. H. MILLS and K. A. ELLIET, *J. Chem. Soc.*, 1928, 1291.
4. B. H. KORSCH and N. V. RIGGS, *Tetrahedron Lett.*, 1966, 5897 ; J. E. ANDERSON and J. M. LEHN, *Tetrahedron*, 1968, **24**, 123.
5. "^{13}C NMR Spectroscopy : Methods and Application in Organic Chemistry", eds. BREITMAIER and VEELTER, 2nd. ed., Verlag Chemie, New York, 1978.
6. D. K. DALLING and D. M. GRANT, *J. Am. Chem. Soc.*, 1967, **89**, 6612.
7. R. K. NORRIS and S. STERNHELL, *Aust. J. Chem.*, 1966, **19**, 617 ; S. KIKKRAWA, M. NOMNRA, Y. UNO, M. MATSUBAR, *Bull. Chem. Soc Jpn.*, 1972, **45**, 2523.
8. R. N. JONES, D. A. RAMSAY, F. HERLING and K. DOBRINGER, *J. Am. Chem. Soc.*, 1952, **74**, 2228.
9. W. ALBREAHT, *Justus Liebigs Ann. Chem.*, 1906, **348**, 31 ; K. ALDER and G. STEIN, *Justus Liebigs Ann. Chem.*, 1933, **501**, 295.
10. R. B. WOODWARD and T. J. KATZ, *Tetrahedron*, 1959, **5**, 70.
11. L. DEVRIES, R. HECK, R. PICCOLINI and S. WINSTEIN, *Chem. Ind. London*, 1959, 1416.
12. F. KAPLAN and H. CONROY, *J. Org. Chem.*, 1963, **28**, 1598.
13. P. D. BARTLETT, M. J. RYAN and S. G. COHEN, *J. Am. Chem. Soc.*, 1942, **64**, 2649.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1038-1043

Synthetic Studies in Diterpene Series. Part X[1]. A Synthesis of 2-Oxygenated (±)-Podocarpa-8,11,13-triene by Transposition of Ketonic Function

DHANONJOY NASIPURI* and SATINATH BANERJEE

Department of Chemistry, Indian Institute of Technology, Kharagpur-721 302

Carbanions generated *in situ* through de-ethoxycarbonylation of ethyl 2-cyano-3,3-dimethyl-5-oxohexanoate (11) and ethyl phenethylcyanoacetate (7) by heating with lithium chloride in hexamethylphosphorus triamide according to Krapcho have been submitted respectively to alkylation reaction with phenethyl bromide and to Michael addition with 4-methylpent-3-en-2-one with a view to utilising the resultant 5-cyano-4,4-dimethyl-7-phenylheptan-2-one (10) for a convenient synthesis of 2-oxopodocarpa-8,11,13-trienes (6). The yields of the reactions are, however, poor (15-20%), presumably due to adverse steric effect of the *geminal* methyl groups in the reactants. Use of sodium hydride under phase transfer catalysis considerably improves the yield of alkylation reaction (with the keto group in 11 protected by cyclic acetal formation) and the product (14) undergoes de-ethoxycarbonylation ; but the resultant nitrile (15) is found to be resistant to hydrolysis leading to an impasse.

2-Oxopodocarpa-8,11,13-triene (20) is finally synthesised from the easily accessible 3-oxo-derivative (18) by transposition of the ketonic function through a two step process, namely oxidation with molecular oxygen in presence of potassium *t*-butoxide to 2,3-dioxo-derivative and its subsequent reduction with boiling hydriodic acid. The ketone (20) on treatment with lithium aluminium hydride affords 2β (axial) and 2α (equatorial) alcohols in a 60 : 40 ratio.

PODOCARPA-8,11,13-triene (1) forms the skeletal structure of a number of naturally occuring ring C-aromatic tricyclic diterpenes and has been synthesised by different groups of workers of which the following may be mentioned : (i) Robinson-Mannich base ring homologation of 3,4-dihydro-1-methylnaphthalen-2(1*H*)-ones followed by dimethylation of the resultant α,β-unsaturated tricyclic ketones and catalytic hydrogenation[2,3] which gives 3-oxopodocarpatrienes (2), useful for synthesis of 3-oxygenated di- and tri-terpenoids ; (ii) cyclisation of 1-phenethyl-2,6,6-trimethylcyclohexanols (3, OH at 1-, 2-, and 3-) and their cyclohexene equivalents[4], an old method recently renovated and improved by Davis *et al.*[5] (use of methane sulphonic acid-phosphorus pentoxide increasing the yield and stereoselectivity) ; and finally, (iii) a biogenetic-type of cyclisation of 6(*E*)-9-aryl-2,6-dimethylnona-2,6-dienes (4)[6] under acid catalysis. Very recently, Bhattacharya and Mukherjee[7] have worked out a synthesis of *cis* 13-methoxy-1-oxopodocarpa-8,11,13-triene starting from a naphthalene derivative and using Birch reduction as a reductive methylation step. In contrast, synthesis of 2-oxopodocarpa-8,11,13-triene system (6) is virtually unknown except for a recent short report by Davis and Johnson[8] who have used copper(I) catalysed 1,6-conjugate addition of methoxybenzylmagnesium chlorides to 4-methylene-3,5,5-trimethylcyclohex-2-enone[9] for the synthesis of cyclohexenones (5) and cyclised them by phosphoric acid into a mixture of 5α- and 5β-2-oxopodocarpa-8,11,13-trienes (6) in a 50 : 50 ratio.

As a part of a programme undertaken in our laboratory for the synthesis of natural products related to diterpenes[10] and furanosesquiterpenes[11], we were interested in developing a simple synthesis of the 2-oxopodocarpatriene system (6) and subsequently utilising it for a total synthesis of salviol, a diterpenoid alcohol with 2α-hydroxy group in a podocarpatriene skeleton, isolated a few years back from *Salvia miltiorrhiza* Bunge[12] (see our synthesis of miltirone[13] isolated from the same species). Our strategy was to prepare the cyclohexenones (5) through a simple sequence of reactions involving

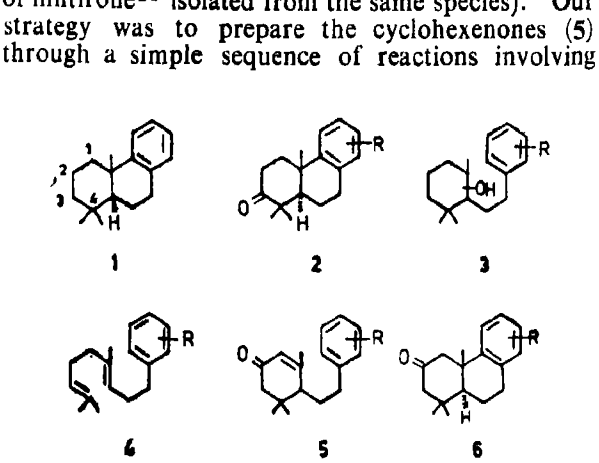
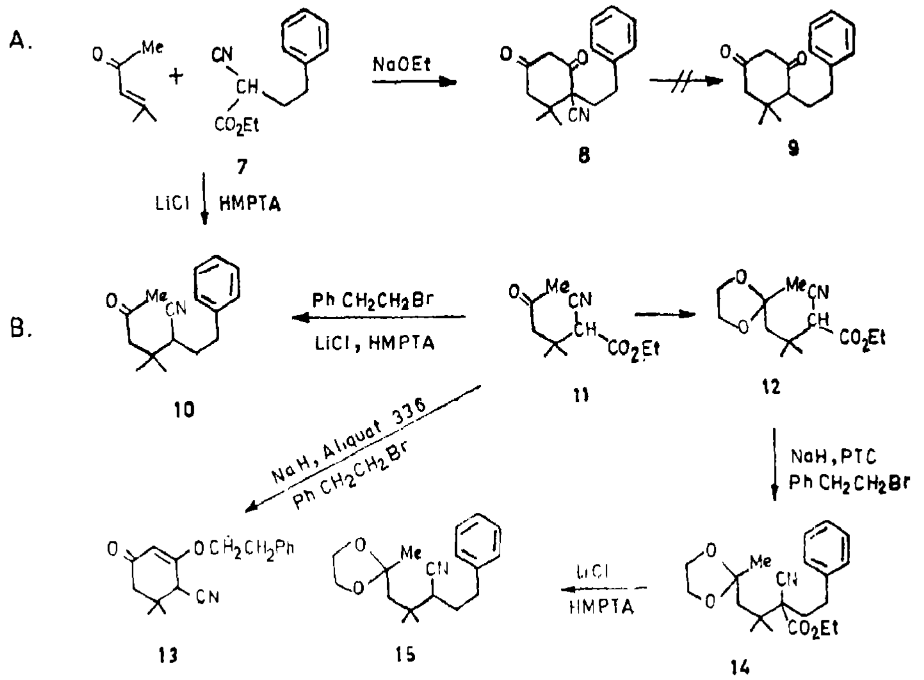


Chart 1

Michael addition of ethyl phenethylcyanoacetate to 4-methylpent-3-en-2-one (mesityl oxide), conversion of the adduct to 5,5-dimethyl-4-phenethyl-

cyclohexa-1,3-dione (9) (Scheme 1A), reaction of methylmagnesium iodide with the derived isobutyl enol ether[14] and acidic hydrolysis to the cyclohexenone (5). The Michael addition, however, did not go even under phase transfer catalysis, a method which we have very successfully used[15] for such reactions using a variety of donor and acceptor molecules. The only product we got was the cyanodiketone (8) which could not be hydrolysed without disrupting the 1,3-dione moiety. In the present communication, we wish to present our results on the generation of carbanions from substituted cyanoacetic esters using Krapcho's techinque[16] (heating with lithium halides in hexmethylphosphorus triamide) and their reactions with Michael acceptors and alkylating agents giving an alternative route to the aforementioned synthon. We also report a clean synthesis of 2-oxopodocarpatriene (20) from the easily accessible 3-oxo-derivative (18) by the transposition of the ketonic function.

Encouraged by these observations, we subjected ethyl phenethylcyanoacetate (7) under the same condition in presence of 4-methylpent-3-en-2-one (Scheme 1B) with the hope that the intermediate α-cyanocarbanion, stripped off the ethoxycarbonyl group and so sterically less hindered and more reactive, would undergo facile Michael addition. Similarly, ethyl 2-cyano-3,3-dimethyl-5-oxohexanoate (11) was allowed to alkylate intermolecularly with phenethyl bromide by heating the reactants with lithium chloride in HMPTA. In both the cases, the expected product, 5-cyano-4,4-dimethyl-7-phenylheptan-2-one (10) was formed but the yields were discouragingly low (15-20%) and the product was contaminated with some amides (ν_{max} 2250, 1718 and 1670 cm^{-1}) presumably due to partial hydrolysis of the cyano group. The major products were those arising out of de-ethoxycarbonylation of the starting cyanoesters. Apparently, the unreactivity of 4-methylpent-3-en-2-one (steric reason)



Scheme 1

Alkylation of the intermediate carbanions in the dealkoxycarbonylation of β-oxoesters, *geminal* diesters and α-cyanoesters by lithium halides in HMPTA has been carried out successfully both intramolecularly[17,18] and intermolecularly[19]. Thus 2-acetobutyrolactone when heated with LiCl in HMPTA affords cyclopropyl methyl ketone (intramolecular decarboxylative alkylation)[17]. Substituted malonic and cyanoacetic esters under similar conditions give mono- and di-alkylated products with alkyl halides accompanied by the loss of a carboethoxyl group (intermolecular alkylation)[19]. A large number of spiro-compounds have also been synthesised[18] from substrates containing both a carboethoxyl group and an alkylating side chain.

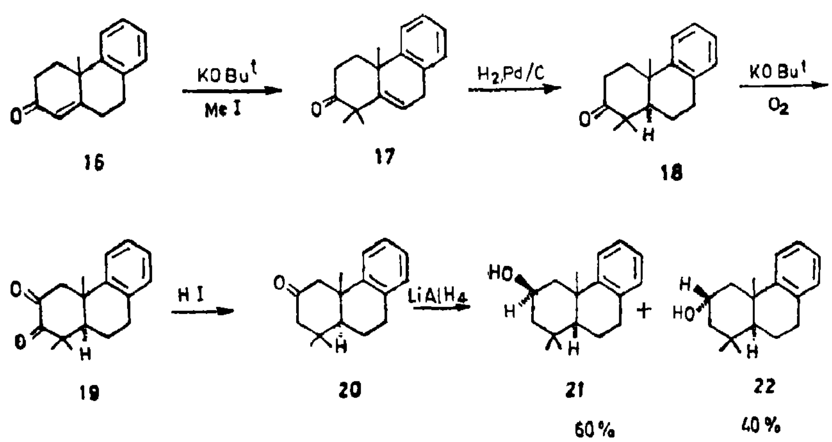
and of phenylethylbromide as an alkylating agent (electronic reason) is responsible for the poor yield. Alkylation of the cyanoester (11) with benzyl chloride under identical condition afforded mono- and di-benzylated products with the loss of ethoxycarbonyl group in 20 and 30% yields, respectively. The yields in all these reactions were not optimised; further study in this direction was abandoned.

A final attempt was made for the alkylation of the substituted cyanoesters (11) and (12) with phenylethyl bromide using sodium hydride and aliquat 336 (tricaprylmethylammonium chloride)[20]. In the first case, the product was a crystalline solid isolated in 75% yield which turned out to be the enol ether (13) (Scheme 1C), obviously formed by

an initial Claisen condensation followed by *O*-alkylation. In the second case, the desired cyano-ester (**14**) was obtained in 45% yield and was smoothly de-ethoxycarbonylated by Krapcho's method. But the resultant cyano-cyclic ketal (**15**) was found to be resistant to hydrolysis leading to another impasse.

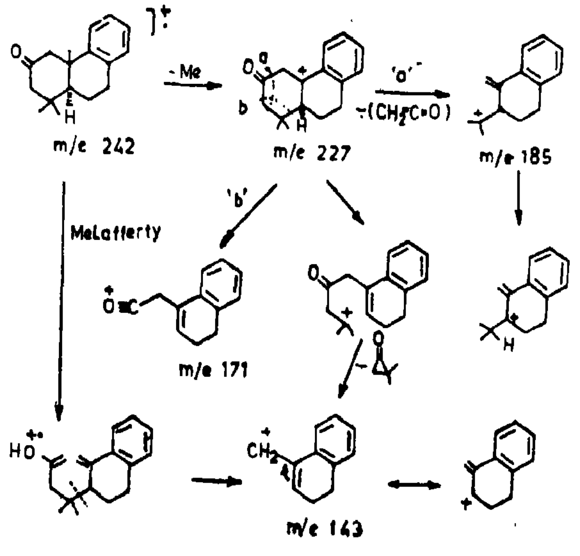
All these attempts having failed, we ultimately took resort to transpose the ketonic function in the easily accessible 3-oxo-podocarpa-8,11,13-triene (**18**) from C-3 to C-2. A large number of methods for such transposition are available depending on the nature of the substrates[21]. Of these we selected the one used for substituted cyclohexanones having

the normal value (δ 1.00) when the ketone (**20**) is reduced to a mixture of alcohols. The mass spectrum of **20** shows specific fragmentations which are discussed in Scheme 3. It differs from that of the 3-oxo-derivative (**18**) in three important aspects: (i) while the spectrum of 2-oxo-compound gives specific fragmentation pattern easily assignable, that of 3-oxo-compound has too many non-specific fragmentations, (ii) the peak at *m/e* 143 in **20** (base peak) is much more intense because of its origin from at least three pathways (Scheme 3) while that in **18** is weak, and (iii) the spectrum of 3-oxo-derivative shows a peak at *m/e* 157, homologous with **23** of *m/e* 143 as expected.



Scheme 2

a quaternary α-carbon which are oxidised[22] by molecular oxygen in presence of potassium *t*-butoxide to α-diketones and then reduced to the isomeric β-quaternary ketone. Accordingly, the tricyclic ketone (**16**)[23] (Scheme 2) was dimethylated[24] to **17**, the latter hydrogenated[25] to the *trans* 3-oxo-derivative (**18**) along with some *cis* isomer[26] (10-15% as determined by glc and ^{1}H nmr[27]). The ketone (**18**) was converted into the diketone (**19**) by oxygenation in basic media and the latter reduced by boiling 47% hydriodic acid to furnish a mixture of two products, the major (the first peak in glc) being the desired 2-oxopodocarpa-8,11,13-triene (**20**) (50%) obtained as a crystalline solid, m.p. 88-90°. The minor contaminant might be 2-hydroxy-3-oxopodocarpatriene and was easily separated out by column chromatography. The 2-oxo-derivative (**20**) showed the ^{1}H nmr spectrum δ ($CDCl_3$) 7.50-7.08 (4H, m, 4×ArH), 2.90 (2H, m, 7-H_2), 2.55 (2H, m, 1-H_2), 2.22 (2H, q, 3-H_2), 1.90 (1H, m, 5 α-H), 1.50-1.20 (2H, m, 6-H_2), 1.33 (3H, s, 10-Me), 1.10 (3H, s, 4 α-Me) and 0.60 (3H, s, 4β-Me). The methylene multiplets and quartets were partly superimposed so that accurate *J* values could not be calculated. The chemical shift of 4-axial methyl protons is unusually upfield and may be due to the anisotropic shielding of the carbonyl group[28,29], an effect perhaps accentuated by 1,3-diaxial interaction between methyl groups. The signal comes down to



Scheme 3

The ketone (**20**) was next reduced with lithium aluminium hydride in ether affording a mixture of 2β-ol (**21**) (60%) and 2α-ol (**22**) (40%). The axial attack leading to equatorial alcohol (**22**) is sterically hindered (see reduction of 3,3,5-trimethylcyclohexa-

none)[20] by two axial methyl groups at C-4 and C-10 and this explains the preponderance of the axial alcohol (**21**) in the reduction. The ratio of the epimeric alcohols in the mixture was determined by glc and supported by ^{1}H nmr spectra which show the methine proton (C*H*OH) as multiplets at δ 3.77 and 4.13 for equatorial and axial alcohols, respectively in 40 : 60 ratio. Pure equatorial (2α-ol) alcohol may be obtained by equilibration of the dichloroalumino derivatives of mixed alcohols[21]. Experiments towards a total synthesis of salviol following this procedure is in progress.

Experimental

All melting points and boiling points are uncorrected. Ir spectra were taken on Perkin-Elmer 237 B infra-cord spectrophotometer, in $CHCl_3$, ^{1}H nmr spectra on a Varian EM 390 90 MHz machine in $CDCl_3$ using $SiMe_4$ as internal standard, and mass spectra with Hitachi RMU-6L spectrometer at 70-80 eV using direct inlet system. Glc was done on a Varian 3700 gas chromatograph using both FFAP (15%) and Carbowax 20M (10%) columns (6′×1/8″) using flame ionisation detector and with N_2 as carrier gas. Light petroleum refers to the fraction b.p. 40-60°. All organic extracts were dried over anhydrous Na_2SO_4. Tlc was done in 20×20 cm plates with 0.1 mm layers of silica gel G.

Ethyl phenethylcyanoacetate (**7**) *:* To the sodiosalt prepared from ethyl cyanoacetate (45.2 g, 0.4 mol) and sodium (4.6 g, 0.2 mol) in dry ethanol (100 ml), was added phenethyl bromide (37.0 g, 0.2 mol) and the mixture refluxed for 12 h. The excess of alcohol was removed under reduced pressure and the product worked up in the usual way to furnish ethyl phenethylcyanoacetate (**7**) (31 g, 79%), b.p. 163-167°/7 mm ; ν_{max} 2250 (CN) and 1750 cm^{-1} (CO_2Et). Attempt to prepare **7** by alkylating ethyl cyanoacetate with phenethyl bromide by heating with anhydrous K_2CO_3 and benzyltriethylammonium chloride (BTEAC) in benzene[16] gave only 35-40% of the product.

Ethyl 2-cyano-3,3-dimethyl-5-oxohexanoate (**11**) *:* Ethyl 2-cyano-3,3-dimethyl-5-oxohexanoate was prepared from 4-methylpent-3-en-2-one and ethyl cyanoacetate by adopting the general procedure of Michael condensation with phase transfer catalyst (BTEAC)[16] in 93% yield. It had b.p. 140°/10 mm.

5-Cyano-4, 4-dimethyl-7-phenylheptan-2-one (**10**) *:* (A) By de-ethoxycarbonylative alkylation—A mixture of ethyl 2-cyano-3,3-dimethyl-5-oxohexanoate (**11**) (10.5 g, 0.05 mol), anhydrous lithium chloride (1.9 g, 0.05 mol) and dry HMPTA (40 ml) was heated in an oil-bath at 150° under nitrogen. When evolution of carbon dioxide ceased (1 h), phenethyl bromide (18.5 g, 0.1 mol) was added dropwise and the mixture stirred at 160° for 6 h. The solution turned into a yellowish red viscous liquid which was cooled, diluted with water, extracted with ether (2×100 ml), the ethereal extract washed thoroughly with water and dried. The residue on evaporation of solvent was distilled *in vacuo*. After an initial low-boiling fraction, (upto 130°/10 mm), a viscous oil was obtained (2.4 g, 20%), b.p. 160-175°/0.5 mm (Found : C, 78.5 ; H, 8.9 ; N, 5.5 . $C_{16}H_{21}NO$ requires C, 79.01 ; H, 8.64 ; N, 5.76%) ; ν_{max} 2250, 1710 and 1670 cm^{-1}. ^{1}H nmr spectrum was more or less consistent with the structure barring two or three extra peaks.

(B) By *in situ* Michael addition—The above experiment was repeated under similar condition with phenethyl bromide replaced by 4-methylpent-3-en-2-one (4.9 g, 0.05 mol). The product on usual work-up and distillation afforded two fractions, (i) b.p. 80-85°/0.4 mm, identified as γ-phenylpropyl cyanide by hydrolysis to γ-phenylbutyric acid, and (ii) b.p. 160-170°/0.4 mm (1.8 g, 15%). The latter was identical (ir) with the one (**10**) described above.

Benzylation of 5-cyano-4,4-dimethyl-7-phenylheptan-2-one : A mixture of the cyanoester (**11**) (8.4 g, 0.04 mol), lithium chloride (1.52 g, 0.04 mol) and HMPTA (20 ml) was heated at 160° for 1 h under nitrogen. Benzyl chloride (5.04 g, 0.04 mol) was added and heating continued for 4 h at 160°. The product on usual work-up afforded 5-cyano-4,4-dimethyl-6-phenylhexan-2-one (1.84 g, 20%), b.p. 135-140°/0.2 mm (Found : C, 78.1 ; H, 8.0 . $C_{15}H_{19}NO$ requires C, 78.6 ; H, 8.3%) ; ν_{max} 2230 and 1705 cm^{-1}. The higher boiling fraction gave 5-benzyl-5-cyano-4,4-dimethyl-6-phenylhexan-2-one (3.8 g, 30%) (Found : C, 82.25 ; H, 7.50. $C_{22}H_{25}NO$ requires C, 82.75 ; H, 7.80%) ; ν_{max} 2200 and 1710 cm^{-1}.

Alkylation of cyano-ester (**11**) *with phenethyl bromide under phase transfer catalysis :* A suspension of sodium hydride (2.5 g, 50% dispersion in oil, 0.05 mol) in a mixture of benzene (50 ml) and dimethylformamide (50 ml) was treated with the cyano-ester (**11**) (10.55 g, 0.05 mol) until evolution of H_2 ceased. Aliquat 336 (1.25 g, 0.0025 mol) in benzene (5 ml) was next added followed by phenethyl bromide (9.25 g, 0.05 mol) and the mixture refluxed with stirring for 20 h. The cooled solution was decomposed with 1 *N* HCl, the organic layer separated and the aqueous phase extracted with ether (2×100 ml). The combined ethereal extract was washed successively with aqueous $NaHCO_3$ and H_2O, dried and solvent evaporated. The residue on distillation afforded a solid (11.1 g, 75%), b.p. 195-205°/0.5 mm, which crystallised from methanol in colourless plates, m.p. 107-109° and identified as 4-cyano-5,5-dimethylcyclohex-2-en-3-yloxyphenethyl ether (**13**) (Found : C, 75.7 ; H, 7.1 ; N, 5.5 . $C_{17}H_{19}NO_2$ requires C, 75.8 ; H, 7.1 ; N, 5.2%) ; ν_{max} 2240 and 1680 cm^{-1} ; δ 7.33 (5H, m, 5×ArH), 5.43 (1H, s, 2-H), 4.07 (2H, t, *J* 7Hz, OCH_2), 3.29 (1H, s, 4-H), 3.00 (2H, t, *J* 7Hz, CH_2Ph), 2.30 (2H, s, 6-H_2), and 1.23 and 1.17 (3H×2, 2×s, 2×CH_3).

Ketalisation of cyano-ester (**11**) *:* A mixture of the cyano-ester (**11**) (21.1 g, 0.1 mol), ethylene

glycol (6.2 g, 0.1 mol), *p*-toluenesulphonic acid (500 mg) and benzene (125 ml) was refluxed with azeotropic separation of water for 20 h. The usual work-up afforded the cyclic ketal (**12**) (20.4 g, 80%), b.p. 135°/8 mm ; ν_{max} 2240 (CN) and 1735 cm^{-1} (CO_2Et) ; δ 4.30 (2H, q, *J* 7Hz, OCH_2), 4.1 (1H, s, C*H*), 4.02 (4H, s, $O-CH_2-CH_2-O$), 1.98 (2H, s, CH_2) and 1.35 - 1.22 (12H, m, 4×CH_3).

Alkylation of cyclic ketal (**12**) *under phase transfer catalysis* : To a suspension of sodium hydride (1.92 g, 50%) in benzene (80 ml) and dimethylformamide (80 ml) was added the ketal (**12**) (10.2 g, 0.04 mol). When the formation of the sodium salt was complete, Aliquat 336 (1.25 g) was introduced in the mixture followed by phenethyl bromide (7.4 g, 0.04 mol). After reflux for 20 h under nitrogen with stirring, the product was decomposed with water containing a few drops of acetic acid, the organic layer separated and the aqueous phase extracted once with benzene. The combined benzene layer was washed with aqueous $NaHCO_3$, dried and distilled. The product (**14**) was collected (6.5 g, 45%), b.p. 160-180°/0.4 mm (Found : C, 69.7 ; H, 8.5. $C_{21}H_{29}NO_4$ requires C, 70.2 ; H, 8.1%); ν_{max} 2230 (CN) and 1735 cm^{-1} (CO_2Et) ; δ 7.31 (5H, br. s, 5×ArH), 4.30 (2H, q, OCH_2), 4.00 (4H, s, $O-CH_2-CH_2-O$), 3.00 (2H, t, $PhCH_2$), 1.94 (2H, s, CH_2), 1.70 (2H, m, CH_2) and 1.33 - 1.10 (12H, m, 4×CH_3).

De-ethoxycarbonylation of cyano-ester (**14**) : A mixture of the above ketal-cyanoester (**14**) (6.0 g, 0.017 mol), lithium chloride (0.65 g, 0.017 mol) and HMPTA (20 ml) was heated at 160° in an oil-bath under N_2 for 3 h till no more CO_2 evolved. The product on usual work-up and distillation afforded the de-ethoxycarbonylated product (**15**) (4.2 g, 85%), b.p. 140-150°/0.5 mm (Found : C, 74.8 ; H, 8.3. $C_{18}H_{25}NO_2$ requires C, 75.3, H, 8.7%) ; ν_{max} 2225 cm^{-1} (CN).

3-Oxopodocarpa-5,8,11,13-tetraene (**17**) : The tricyclic ketone (**16**), m.p. 91°, was prepared from 3,4-dihydro-1-methylnaphthalen-2(1*H*)-one by the usual method[28]. To a solution of potassium *t*-butoxide prepared from potassium (1.6 g, 0.043 mol) and dry *t*-butanol (75 ml) was added a solution of the ketone (**16**) (3.1 g, 0.145 mol) in benzene (5 ml). A reddish colour appeared ; methyl iodide (10.3 g) was added and the mixture stirred overnight at ambient temperature. It was then decomposed with water and a few drops of HCl, the organic matter extracted with ether, dried and distilled. A viscous oil obtained (2.5 g, 70%), b.p 160-165 /1 mm was purified by chromatography over silica gel (100 g). Although glc of the purified sample gave a single peak, the compound (**17**) could not be crystallised (Found : C, 84.8 ; H, 8.6. $C_{17}H_{20}O$ requires C, 85.0 ; H, 8.33%) ; ν_{max} 1705 cm^{-1} ; δ 7.30 (4H, m, 4×ArH), 6.0 (1H, t, *J* 4.5 Hz, 6 H), 3.40 (2H, d *J* 4.5 Hz, 7-H_2), 2.70-2.20 (4H, m, 2×CH_2) and 1.32, 1.23 and 1.13 (9H, 3×s, 3×CH_3).

3-Oxopodocarpa-8,11,13-triene (**18**) : The foregoing unsaturated ketone (**17**) (2.0 g) in ethanol (30 ml) was shaken in an atmosphere of H_2 with palladium-charcoal (500 mg) for 10 h during which time theoretical amount of H_2 was absorbed. The catalyst was filtered off and the resultant 3-oxopodocarpatriene (**18**) was worked up and distilled (1.8 g), b.p. 135-145°/0.5 mm. Glc and ^{1}H nmr showed it to be a mixture of 5α (>80%) and 5β (<20%) isomers. It was purified by column chromatography over silica gel when 5α-isomer was obtained (1.00 g) (Found : C, 84.0 ; H, 9.5. $C_{17}H_{22}O$ requires C, 84.3 ; H, 9.1%) ; ν_{max} 1705 cm^{-1} ; δ 7.30 (4H, m, 4×ArH), 2.88 (2H, t, 7-H_2), 2.53 (2H, m, 2-H_2), 2.00-1.30 (5H, m, 2×CH_2+CH) and 1.23-1.07 (9H, 3×s, 3×CH_3) ; *m/e* 242 (M^+), 227, 185, 157, 143 and 129 (peaks with lower *m/e* values not given).

2-Oxopodocarpa-8,11,13-triene (**20**) : (A) Oxidation of the 3-oxoderivative—The foregoing ketone (**18**) (0.4 g) in dry *t*-butanol (40 ml) containing potassium *t*-butoxide made to 1 *N* was shaken in oxygen for 20 min. Water (5 ml) and acetic acid (5 ml) were added and *t*-butanol was removed *in vacuo*. The residue was extracted with ether. The ethereal solution was washed successively with aqueous $NaHCO_3$, 20% KOH and H_2O, dried and solvent removed to furnish the diketone (**19**) as an oily residue (0.4 g) which was submitted to the next operation without further purification.

(B) Reduction of the dioxo-compound (**19**)—The above diketone (**19**) was heated with a refluxing mixture of glacial acetic acid (25 ml) and aqueous HI (47%, 5 g) for 2 h. The mixture was diluted with water, the organic matter taken up in ether, the ethereal solution washed with aqueous NaOH, dried and solvent removed. The dark-coloured residue was passed through a column of silica gel and analysed by glc which showed two peaks with 70 : 30 ratio having retention times of 32 and 39 min, respectively (FFAP column at 220°). The two components were easily separated by column chromatography using silica gel and the first eluent was identified as 2-oxopodocarpa-8,11,13-triene (**20**) (120 mg), m.p. 88-90° (Found : C, 84.1 ; H, 9.4. $C_{17}H_{22}O$ requires C, 84.3 ; H, 9.1%) ; ν_{max} 1710 cm^{-1}. The ^{1}H nmr and mass spectra have been already discussed.

Reduction of 2-oxopodocarpa-8,11,13-triene (**20**) : The above ketone (50 mg) was added to an ethereal solution (1 ml, 1 *M*) of $LiAlH_4$. After agitation for 0.5 h, the solution was decomposed with cold 4 *N* H_2SO_4 and the product taken up in ether. On removal of the solvent, the mixture of 2β (**21**) and 2α (**22**) alcohols was obtained as a colourless gum. It was analysed by glc, the results of which have already been discussed. No attempt was made at this stage to separate the two epimeric alcohols. The mixture showed ^{1}H nmr spectrum as follows : δ 7.30 (4H, m, ArH), 4.13 (0.6H, m, 2-H_α), 3.77 (0.4H, m, 2-H_β), 2.80 (2H, m, 7-H_2), 2.30-1.80 (4H, m, 2×CH_2), 1.82-1.30 (3H, m, CH_2+CH) and 1.25-1.00 (9H, m, 3×CH_3).

Acknowledgement

One of the authors (S.B.) is grateful to C.S.I.R., New Delhi for a Senior Fellowship. The authors wish to record their thanks to Dr. Esak Ali, I.I.C.B., Calcutta for helping in the mass spectral analysis. The ^{1}H nmr spectra were recorded by Shri N. P. Daw, Department of Chemistry, I.I.T., Kharagpur.

References

1. Part-IX, D. NASIPURI, I. DE DALAL and D. N. ROY, *J. Chem. Soc., Perkin Trans.* 1, 1973, 1754.
2. K. RAMAN and P. N. RAO, *Tetrahedron*, 1958, **4**, 294 ; see also E. C. DU FEU, F. J. McQUILLIN and R. ROBINSON, *J. Chem. Soc.*, 1937, 58.
3. G. STORK, A. MEISELS and J. E. DAVIES, *J. Am. Chem. Soc.*, 1963, **85**, 3419.
4. T. MATSUMOTO and S. USUI, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 212.
5. B. W. AXON, B. R. DAVIS and P. D. WOODGATE, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2956 and references therein.
6. D. NASIPURI, *J. Indian Chem. Soc.*, 1963, **40**, 407 ; D. NASIPURI, R. BHATTACHARYA and C. K. GHOSH, *J. Chem. Soc.* (C), 1969, 782.
7. S. BHATTACHARYA and D. MUKHERJEE, *Tetrahedron Lett.*, 1982, 4175.
8. B. R. DAVIS and S. J. JOHNSON, *J. Chem. Soc., Chem. Commun.*, 1978, 614.
9. B. R. DAVIS and S. J. JOHNSON, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2840.
10. D. NASIPURI and M. GUHA, *J. Chem. Soc.*, 1962, 4248 ; D. NASIPURI and I. DE DALAL, *J. Chem. Soc., Perkin Trans. 1*, 1976, 19.
11. D. NASIPURI and G. DAS, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2776.
12. T. HAYASHI, T. HANDA, M. OHASHI, K. KAKISAWA, HONG-YEN HSU and YUH PAN CHEN, *J. Chem. Soc., Chem. Commun.*, 1971, 541.
13. D. NASIPURI and A. K. MITRA, *J. Chem. Soc., Perkin Trans. 1*, 1973, 285.
14. G. PYNE, R. C. BANERJEE and D. NASIPURI, *J. Indian Chem. Soc.*, 1963, **40**, 199 ; R. L. FRANK, R. ARMSTRONG, J. KWIATEK and H. A. PRICE, *J. Am. Chem. Soc.*, 1948, **70**, 1379.
15. S. BANERJEE, M. DATTA GUPTA, A. SARKAR and D. NASIPURI, *J. Indian Chem. Soc.*, 1983, **60**, 1163.
16. A. P. KRAPCHO, J. F. WEIMASTER, J. M. ELDRIDGE, E. G. E. JAHNGEN, A. J. LOVEY and W. P. STEPHENS, *J. Org. Chem.*, 1978, **43**, 138.
17. S. TAKEI and Y. KAWANO, *Tetrahedron Lett.*, 1975, 4389.
18. R. G. EILERMAN and B. J. WILLS, *J. Chem. Soc., Chem. Commun.*, 1981, 30.
19. A. MORIO, M. KAZUTOSHI and T. HISASHI, *Chem. Lett.*, 1975, 1149.
20. H. D. DURST and L. LIEBESKIND, *J. Org. Chem.*, 1974, **39**, 3271.
21. F. M. HAUSER and S. PRASANNA, *Synthesis*, 1980, 621 ; E. J. COREY and J. E. RICHMAN, *J. Am. Chem. Soc.*, 1970, **92**, 5276 ; B. M. TROST, K. HIROI and S. KUNOSUMI, *J. Am. Chem. Soc.*, 1975, **97**, 438 ; W. E. FRISTAD, T. R. BAILEY and L. A. PAQUETTE, *J. Org. Chem.*, 1978, **43**, 162 ; J. A. MARSHALL and H. ROEBKE, *J. Org. Chem.*, 1969, **34**, 4188 and references therein.
22. W. REUSCH and R. LEMAHIEU, *J. Am. Chem. Soc.*, 1964, **86**, 3068 ; E. BAILEY, D. H. R. BARTON, J. ELKS and J. F. TEMPLETON, *J. Chem. Soc.*, 1962, 1578.
23. K. D. ZWAHLEN, W. J. HORTON and G. FUJIMOTO, *J. Am. Chem. Soc.*, 1957, **79**, 3131.
24. M. YANAGITA, M. HIRAKURA and F. SEKI, *J. Org. Chem.*, 1958, **23**, 841.
25. H. J. RINGOLD and G. ROSENKRANZ, *J. Org. Chem.*, 1957, **22**, 602.
26. Y. TACHIBANA, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 298.
27. M. FETIZON and G. MOREAU, *Bull. Soc. Chim. Fr.*, 1965, 3479.
28. L. M. JACKMAN and S. STERNHELL, "Applications of NMR Spectroscopy in Organic Chemistry", Pergamon Press, Oxford, 1969, p. 243.
29. D. NASIPURI, A. K. SAMADDAR and G. DAS, *Indian J. Chem., Sect. B*, 1980, **19**, 727.
30. P. T. LANSBURY and R. E. MACLEAY, *J. Org. Chem.*, 1963, **28**, 1940.
31. E. L. ELIEL and D. NASIPURI, *J. Org. Chem.*, 1965, **30**, 3809.
32. See also M. FETIZON and J. DELOBELLE, *Bull. Soc. Chim. Fr.*, 1961, 1632.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1044-1047

Physico-Chemical Studies of Catechins and Epicatechins

JOGINDER SINGH and N. K. RALHAN*

Department of Chemistry, Punjabi University, Patiala-147 002

and

T. K. PANT

Sri Ganesh Research Institute, A-9, Meerut Road, Ghaziabad

The physico-chemical properties of (−)-epicatechin, (+)-catechin have been found to be at variance from those reported in literature, and have been corrected after confirmation, by elemental analysis, TGA *etc.* A quasiracenate ($C_{15}H_{14}O_6.3H_2O$) of (−)-epicatechin and (+)-catechin (1 : 1) has also been isolated and characterised.

IN India more than one million tons of heartwood of *Acacia catechu* (wild), is processed annually for obtaining pale catechu *(Katha)* and cutch. And yet it is a bit strange that (−)-epicatechin (for which *Acacia catechu* wild is the richest source) is not available in quantities enough to conduct clinical trials. Obviously, this prompted us to conduct a thorough search of the literature for a good preparative method, but with little success. The patent of Karnik and Sharma[1] describes a method, which gives a product containing not more than 85% purity with respect to catechins. Rather, we came across a large number of conflicting and contradictory reports.

In this paper we wish to rationalise the transformations of epicatechins and catechins along with their physical characteristics. The physical characteristics for the isomeric catechins given in the literature[2,3] (Table 1), have been found to be at variance from our study as confirmed by both elemental and thermogravimetric analysis of (−)-epicatechin, (+)-catechin and (±)-catechin. This study has further helped in developing for the first time the commercial production methods for these three isomeric products and have been applied for patents[4].

Results and Discussion

Thermogravimetric and elemental analysis of catechins ($C_{15}H_{14}O_6.xH_2O$): (−)-Epicatechin (2R, 3R) *cis* form, after crystallisation from water and drying in air at room temperature or in a dessicator over fused calcium chloride, did not contain any water of crystallisation (x = zero) and melts at 242-44°. Thermogravimetric measurements (Fig. 1) confirmed this. (−)-Epicatechin is extremely stable and the first fragmentation starts only above 300°. In amber coloured and closed containers it did not change colour or physical characteristics for over 3 years.

(+)-Catechin (2R, 3S) *trans* form, when freshly crystallised and air dried at room temperature is a tetrahydrate and melts at 97°. The tetrahydrate (x = 4) on drying over fused calcium chloride loses two of its water molecules (2-5 days, depending

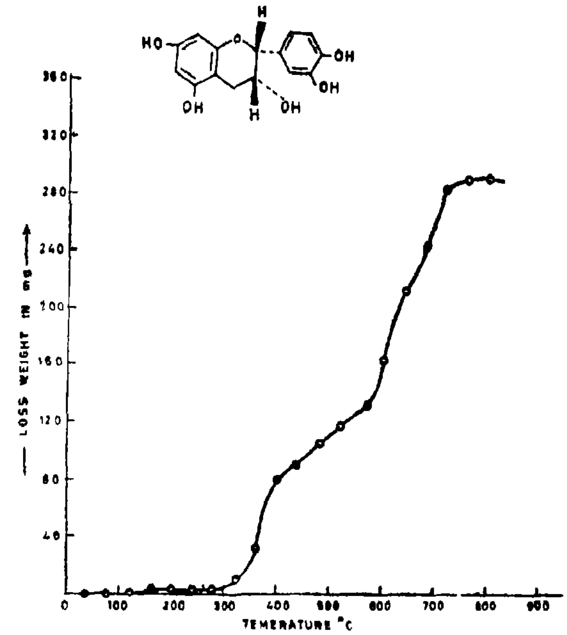


Fig. 1. Thermogram of (−)-epicatechin O. *Cis* (2R, 3R) form.

upon environmental temperature) and a stable dihydrate (x = 2) is obtained with a melting point of 174-76°. Drying at 80-85° produces anhydrous (+)-catechin (x = zero) which melts at 209-10°. Slow heating during the determination of melting points also dehydrates it and melts at 209-10°. The TGA (Fig. 2) further confirms that the dehydration of dihydrate of (+)-catechin starts around 60° and completes at 200°. The residual product does not decompose earlier than 260°, which is far above its melting point. Again, the dihydrate has a tendency to gain water and to change to tetrahydrate under high humidity condition (RH above 50%).

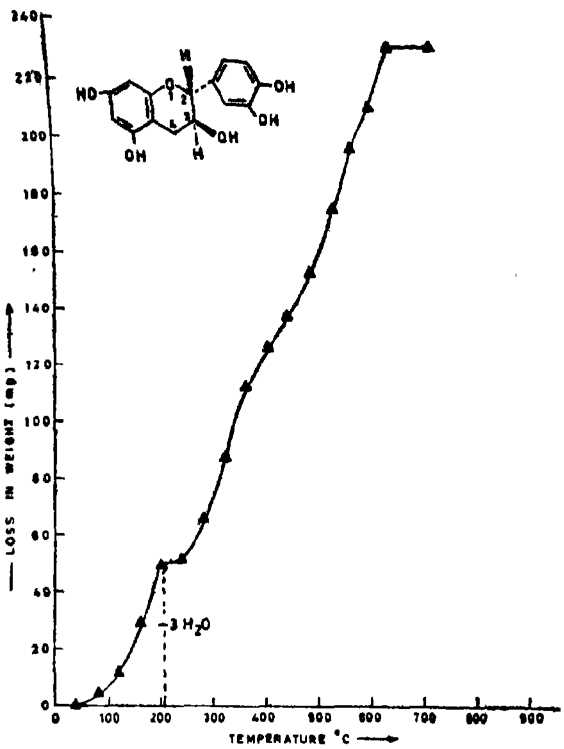


Fig. 2. Thermogram of (+)-catechin ▲. *Trans* (2R, 3S) form.

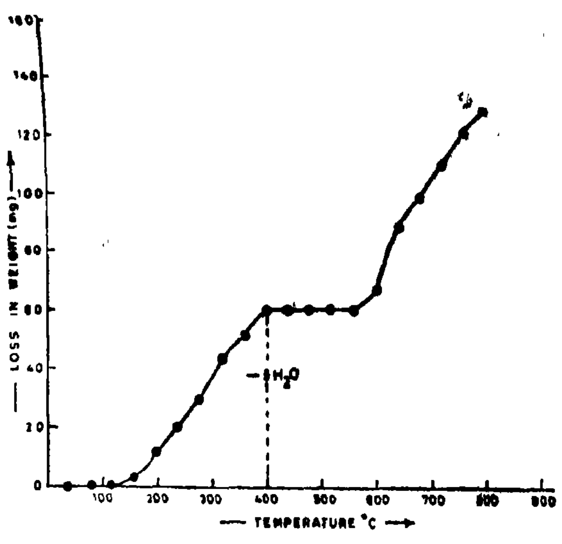


Fig. 3. Thermogram of (±)-catechin ●.

(±)-Catechin, the racemate, crystallises as a very stable trihydrate (x = 3), which does not show any tendency to lose the water of crystallisation and melts at 210-12°. Its mixed melting point with (+)-catechin is 144-48°. The TGA (Fig. 3) indicates that the dehydration did not start before 150° and followed a continuous loss (−3H_2O) upto 375°. The residue is stable upto 575°.

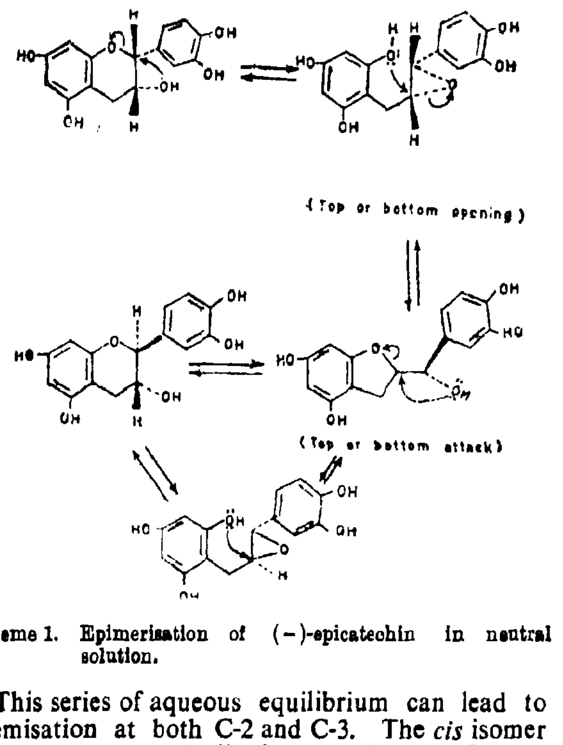
(±)-Catechin (racemate of *trans* form) is the chief constituent (30-60%) along with tannins, of the trade product-pale catechu *(Katha)*, which is the conversion product of (−)-epicatechin. The information about the transformation of (−)-epicatechin to (±)-catechin is quite sketchy and the mechanism is not fully understood. Along with fresh studies we have repeated some of the literature reports and concluded that all the isomeric catechins are very prone to transformations and polymerisation under alkaline conditions. Epicatechins (with *cis* configuration) have a much lower life time than the catechins (with *trans* configuration). Pedersen *et al.*[5], even with fast speed esr studies, failed to note any special characteristics for (−)-epicatechin (2R, 3R form). The esr spectra of oxygen saturated alkaline solutions of (−)-epicatechin did not differ from that of (+)-catechin. Under the alkaline conditions, as reported by Sears *et al.*[6] all the isomeric catechins transform themselves to catechinic acid, 6-(3',4'-dihydroxyphenyl)-7-hydroxy-2,4,9-bicyclo [3,

TABLE 1—CORRECTED PHYSICAL CONSTANTS OF CATECHINS

Sl. no.	Substance	Molecular formula	M.p.	R_f*	Analysis % : Found/(Calcd.) C	H
1.	(−)-Epicatechin	$C_{15}H_{14}O_6.4H_2O$	245*a	—	—	—
		$C_{15}H_{14}O_6$	242-44*b	0.65	62.585 (62.07)	4.782 (4.83)
2.	(+)-Catechin	$C_{15}H_{14}O_6.4H_2O$	96*a	—	—	—
			97*b	0.72	49.65 (49.72)	5.95 (6.07)
		$C_{15}H_{14}O_6.2H_2O$	177*b	—	54.616 (55.21)	5.578 (5.52)
		$C_{15}H_{14}O_6$	177*a	—	—	—
			209-10*b	—	62.34 (62.07)	4.94 (4.83)
3.	Quasiracemate of (−)-epicatechin and (+)-catechin (1 : 1)	$C_{15}H_{14}O_6.3H_2O$	178*b	0.85	52.192 (52.82)	5.504 (5.81)

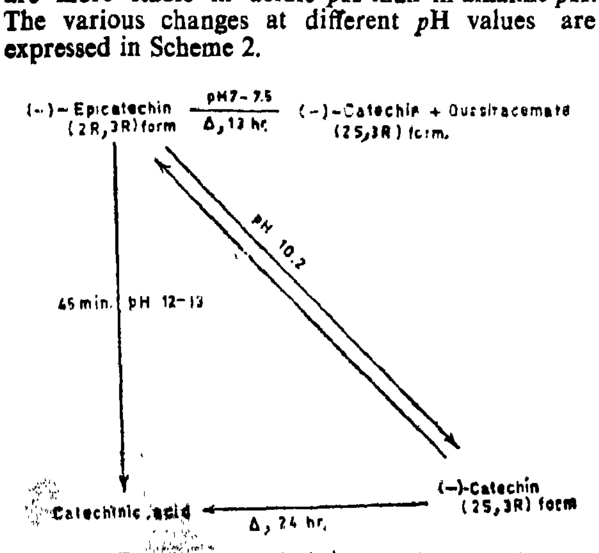
* On Whatman filter paper No. 1 strips using lower layer of n-BuOH : AcOH : H_2O (4 : 1 : 5).
a Refs. 2 and 3. b Present work.

3,1] nonatrione in oxygen-free alkaline solutions. Freudenberg and Purmann[7] have noted the epimerisation of (+)-catechin to (+)-epicatechin in potassium carbonate solution (*p*H 10.2). We have found that all the catechins on prolonged heating in aqueous carbonate solutions turn to catechinic acid. The study of boiling catechins in neutral aqueous solutions is far more interesting. The course of the reaction was followed by paper chromatography and the proposed mechanism is given in Scheme 1.



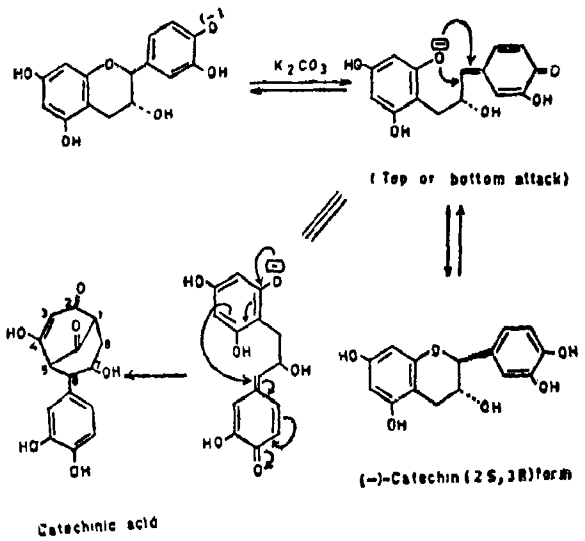
Scheme 1. Epimerisation of (–)-epicatechin in neutral solution.

This series of aqueous equilibrium can lead to racemisation at both C-2 and C-3. The *cis* isomer being thermodynamically less stable transformed into more stable *trans* isomers. The mechanism finds ample support from the fact that epicatechins are more stable in acidic *p*H than in alkaline *p*H. The various changes at different *p*H values are expressed in Scheme 2.



Scheme 2. Transformations in (–)-epicatechins at various *p*H values.

The mechanism of the transformation in neutral media has been given earlier. The mechanism for the transformation at slightly alkaline *p*H range is given in Scheme 3.



Scheme 3. Mechanism of epimerisation and formation of catechinic acid from (–)-epicatechin in alkaline *p*H.

The R_f values on using the lower phase of n-BuOH : AcOH : H_2O (4 : 1 : 5) as elution solvent for (–)-epicatechin, (+)-catechin, (±)-catechin and a quasiracemate were 0.65, 0.72, 0.74 and 0.85, respectively. The quasiracemate ($C_{15}H_{14}O_6.3H_2O$) is a 1 : 1 mixture of (–)-epicatechin (2R, 3R) form and (+)-catechin (2R, 3S) form. On boiling (–)-epicatechin in aqueous NaOH solutions (*p*H 12-13), catechinic acid is formed, whereas an aqueous solution of K_2CO_3 is more suitable for epimerization of (–)-epicatechin (2R, 3R) form to (–)-catechin (2S, 3R) form. On prolonged heating it transforms itself to thermodynamically more stable product, catechinic acid[6]. In neutral solutions (*p*H 7-7.5) along with epimerization there is a pronounced racemisation at both C-2 and C-3. The epimerisation of (–)-epicatechin (2R, 3R) form to (–)-catechin (2S, 3R) form and *vice versa* and the formation of catechinic acid is explained in Scheme 3. On the other hand, the process of racemisation at both C-2 and C-3 can be visualised through a series of aqueous equilibria (Scheme 1).

Quasiracemate of (–)-epicatechin (2R, 3R) form and (+)-catechin (2R, 3S) form : quasiracemate (R_f 0.85) was for the first time isolated on cooling the neutral aqueous solution of (–)-epicatechin, which had been boiled for 13 h, and its structure confirmed by a systematic study, where only stoichiometric quantities of (–)-epicatechin and (+)-catechin on crystallisation from water produced a trihydrate of quasiracemate with a sharp melting point of 178°. The sane quasiracemate also separates out when (–)-epicatechin was added to a saturated aqueous solution of (±)-catechin, (–)-catechin remained in the mother liquor.

Experimental

Thermogravimetric measurements : The catechins used were pure with respective sharp melting points, and correct C, H analyses carried out in Chemistry Department, Punjabi University, Patiala. The thermoanalytical measurements were carried out in Chemistry Department, Guru Nanak Dev University, Amritsar ; the furnace temperature was raised at the rate of $\sim 10^\circ$ min^{-1}. The instrument recorded simultaneously the temperature (t) and weight (t_g) of the substance at that temperature.

Chromatographic studies : The paper chromatography was carried out on strips of Whatman filter paper No. 1, using the lower phase of n-butanol : acetic acid : water (4 : 1 : 5). The R_f values for (–)-epicatechin, (–)-catechin or (+)-catechin, (±)-catechin and quasiracemate were 0.65, 0.72, 0.75 and 0.85, respectively.

Epimerization of (–)-epicatechin (2R, 3R) form to (–)-catechin (2S, 3R) form and catechinic acid : The aqueous solution of (–)-epicatechin (20 g), K_2CO_3 (0.015 g) and water (15 ml) was heated on a steam bath and course of the reaction checked by paper chromatography, drawing a sample every hour. Epimerization started during the first hour, and an equilibrium was established in 3 h. Catechinic acid formation started after 4 h.

Racemization of (–)-epicatechin at both C-2 and C-3 : (–)-Epicatechin (5.0 g) was dissolved in water (100 ml) and heated in a steam bath. The samples were drawn hourly and checked by paper chromatography. The formation of both (–)-catechin and quasiracemate started in 1 h. (–)-Epicatechin was completely transformed in 13 h refluxing in water.

Quasiracemate : (A) The stoichiometric mixture of (–)-epicatechin and (+)-catechin (2.0 g each) on crystallisation from water gave a crystalline substance, m.p. 178° (Found : C, 52.192 ; H, 5.504. $C_{15}H_{14}O_6.3H_2O$ calcd. C, 52.32 ; H, 5.81%). The excess of either one was retained in the mother liquor.

(B) A solution of (±)-catechin (4.0 g) and (–)-epicatechin (1.0 g) in boiling water was allowed to cool. The crystals which separated out were those of quasiracemate and were identical with those obtained under (A) (R_f 0.85). The mother liquor contained (–)-catechin (R_f 0.72).

Acknowledgement

The authors are thankful to the U.G.C., New Delhi for providing fellowship (J.S.).

References

1. M. G. KARNIK and O. P. SHARMA, Indian Pat., 91, 662/1966 (*Chem. Abstr.*, 1969, **70**, 39055).
2. I. HEILBRON and H. M. BURNBURY, "Dictionary of Organic Compounds", Erye and Spottiswoode, London, 1965, Vol. I, p. 572.
3. Thorpe's Dictionary of Applied Chemistry, 4th. ed., Longman Green, London, 1938, Vol. II, p. 486.
4. K. S. NARANG, N. K. RALHAN, M. L. PARMAR, A. N. KAUSHAL, J. S. SODHI, T. K. PANT and R. P. S. TEOTIA, Indian Pat. Appl. 71/DEL/83 ; 72/DEL/83 ; 73/DEL/83.
5. O. N. JENSEN and J. A. PEDERSEN, *Tetrahedron*, 1983, **39**, 1609.
6. K. D. SEARS, R. L. CASEBIER and H. L. HERGERT, *J. Org. Chem.*, 1974, **39**, 3244.
7. K. FREUDENBERG and L. BURMANN, *Ann.*, 1924, **437**, 274.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1048-1049

Synthesis of *N*-Allyl-2-oxocycloalkanecarbothioamides, Functionalised Organic Intermediates *via* Enamines

HARJIT SINGH*, PARAMJIT SINGH and R. K. MEHTA

Department of Chemistry, Guru Nanak Dev University, Amritsar-143 005

Cyclopent-1-enylmorpholine (1a)/pyrrolidine (1b) and cyclohex-1-enylpyrrolidine (1c)/aniline (1d) with allyl isothiocyanate furnish *N*-allyl-2-oxo-cyclopentane- and *N*-allyl-2-oxocyclohexanecarbothioamides (3, n=3/4), respectively after hydrolysis of the product mixture.

THE carbothioamide intermediates (**2**, R=alkyl, aryl, acyl and aroyl), formed as 1 : 1 adducts in the reactions of enamines (**1**) and isothiocyanates through the interaction of enamine β-carbon and isothiocyanato carbon are useful in the synthesis of a variety of heterocyclic systems[1,2]. The presence of allyl group in such compounds (**2**, R=allyl) would be of enhanced synthetic consequence. Earlier, we found that allyl isothiocyanate, contrary to literature reports[1,2], reacts at $-NH_2$ and not at enamine β-carbon of ethyl β-aminocrotonate[3]. Here, we report that more reactive enamines, *viz.* cycloalk-1-enylamines (**1**) in their reactions with allyl isothiocyanate reacts at enamine β-carbon to provide *N*-allyl-2-oxocycloalkanecarbothioamides (**3**) through the hydrolysis of initially formed adduct (**2**, R=allyl).

Cyclopent-1-enylmorpholine (**1a**) with allyl isothiocyanate at room temperature gives a product mixture consisting of three components, A, R_f 0.70 ; B, R_f 0.60 and C, R_f 0.30 ($CHCl_3$: EtOH, 95 : 5). The component A during chromatography changed to the component B. The component B obtained as a dark brown liquid in its mass spectrum shows the parent ion peak M^+ m/z 183 (M.F. $C_9H_{13}NOS$). Its pmr spectrum shows the signals at δ 1.75-2.8 (m, 6H) and 3.5-3.9 (m, 1H) (monosubstituted cyclopentanone ring H), 4.3 (d, 2H, $-CH_2-$), 5.0-6.2 (m, 3H, $-CH=CH_2$) and 8.85 (1H, NH exchangeable with D_2O) and the ir bands appear at 3250 (NH) and 1705 cm^{-1} (C=O). On the basis of these spectral data, it has been assigned the structure *N*-allyl-2-oxocyclopentanecarbothioamide (**3**, n=3). Component C has been found to be identical (R_f and m.m.p.) with an authentic sample of *N*-allyl-morpholine-1-carbothioamide (**4**)[4].

It was argued that component A might be *N*-allyl-2-(1-morpholinyl)-1-cyclopentene-1-carbothioamide (**2a**, R=allyl) which on chromatography hydrolysed to (**3**, n=3). Alternatively, the crude product mixture was hydrolysed with 4 *N* HCl and after work-up it consisted of only (**3**, n=3) and (**4**).

Similarly, the reactions of cyclopent-1-enylpyrrolidine (**1b**) and cyclohex-1-enylpyrrolidine (**1c**) with allyl isothiocyanate furnished (**3**, n=3) and (**3**, n=4), respectively alongwith *N*-allyl-pyrrolidine-carbothioamide (**5**). Cyclohex-1-enylaniline (**1d**) with allyl isothiocyanate provided (**3**, n=4) and *N*-phenyl-*N*-allyl thiourea (**6**).

Hence, unlike ethyl β-aminocrotonate, cycloalk-1-enylamines (**1**) react with allyl isothiocyanate at enamine β-carbon, and the adducts (**2**, R=allyl) thus formed hydrolyse to the corresponding *N*-allyl-2-oxocycloalkenecarbothioamide derivatives (**3**) which constitute functionalised organic intermediates of potential synthetic utility. The *N*-allyl carbothioamide derivatives (**4**, **5** and **6**) of amines might be formed from the free amine present as an impurity in the enamine.

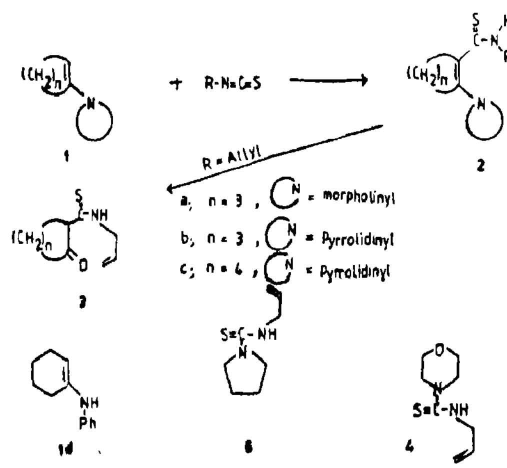
Experimental

Melting points were determined in capillaries and are uncorrected. Pmr spectra were recorded on Tesla BS 487C 80MHz instrument using TMS as internal standard. Ir spectra were recorded with CZ specord-7 spectrophotometer. Mass spectra were run on Hitachi-Perkin-Elmer RMU-60D instrument. For tlc, plates coated with silica gel G were run in chloroform and the spots were developed in an iodine chamber.

Reaction of cyclopent-1-enylmorpholine (**1a**) *with allyl isothocyanate :* (i) A mixture of cyclopent-1-enylmorpholine (1.53 g, 0.01 mol) and allyl isothiocyanate (0.99 g, 0.01 mol) was stirred at room temperature under anhydrous condition. The progress of the reaction was monitored through tlc, and completed after 1 h. The reaction mixture consisted of three components A, R_f 0.70 ; B, R_f 0.60 and C, R_f 0.30. ($CHCl_3$: EtOH, 95 : 5). The product mixture was chromatographed over neutral alumina using benzene as eluent and component A could not be isolated. Component B, *N*-allyl-2-oxocyclopentanecarbothioamide (**3** n=3) was isolated as a dark brown liquid (85)%. Component C, *N*-allyl-morpholine-1-corbothioamide (**4**), m.p. 53-54°, was found to be identical with an authentic sample of (**4**)[4].

(ii) In a separate reaction, the solution of the crude product mixture in 4 *N* HCl, was heated on a water bath. The reaction was monitored by tlc of aliquot portions of the reaction mixture drawn at regular intervals for the disappearance of component A which took 1 h. The reaction mixture was basified with aqueous sodium bicarbonate and extracted with chloroform. The extract was dried (Na_2SO_4), solvent distilled off and the residue consisted of *N*-allyl-2-oxo-cyclopentanecarbothioamide (**3**, n = 3), (90%) and *N*-allyl morpholine-1-carbothioamide (**4**) which were isolated by column chromatography.

The following reactions were performed in a similar manner and the product mixtures were hydrolysed. The products were isolated by column chromatography over neutral alumina using benzene as eluent.



Reaction of cyclopent-1-enylpyrrolidine (**1b**) *and allyl isothiocyanate :* The reaction gives (i) *N*-allyl-2-oxocyclopentanecarbothioamide (**3**, n = 3) (85%), and (ii) *N*-allyl-pyrrolidine-1-carbothioamide (**4**), m.p. 61-2° (Found : N, 5.52. $C_8H_{14}N_2S$ requires N, 16.46%) ; δ($CDCl_3$) 2.05 (4H, m) and 3.66 (4H, m) (Pyrrolidine H), 4.21 (2H, d, $-CH_2-$), 5.05 (3H, m, $-CH=CH_2$).

Reaction of cyclohex-1-enylpyrrolidine (**1c**) *and allyl isothiocyanate :* The reaction gives (i) *N*-allyl-2-oxocyclohexanecarbothioamide (**3**, n = 4) (90%), a dark brown semi-solid ; ν_{max} 3350, 2925, 1705, 1660, 1640, 1600, 1560, 1370, 1350, 1330, 1290 cm^{-1}, δ($CDCl_3$) 1.15-2.5 and 2.7 (9H, cyclohexanone H), 4.22 (2H, d, $-CH_2-$), 5.0-6.2 (3H, m, $-CH=CH_2$), 9.6 (1H, NH, exchangeable with D_2O) ; $M^{+\cdot}$ *m/z* 197 (M.F. $C_{10}H_{15}NOS$), and (ii) *N*-allyl-pyrrolidine-1-carbothioamide (**5**).

Reaction of cyclohex-1-enylaniline (**1d**) *and allyl isothiocyanate :* The reaction gives (i) *N*-allyl-2-oxocyclohexanecarbothioamide (**3**, n = 4,) (80%), and (ii) *N*-phenyl-*N*-allyl thiourea (**6**).

Acknowledgement

The authors thank Prof. P. T. Manoharan for mass spectra and the C. S. I. R. New Delhi for financial assistance.

References

1. H. ULRICH, "Cycloaddition Reactions of Heterocummulenes", Academic Press, New York, 1967, p. 220.
2. G. DE STEVENS, H. M. BLATTER and R. W. J. CORNEY, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 35.
3. H. SINGH, S. SINGH and R. K. MEHTA, *Indian J. Chem., Sect B*, 1976, **14**, 215.
4. R. A. HENRY and W. M. DEHN, *J. Am. Chem. Soc.*, 1950, **72**, 2806.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1050-1052

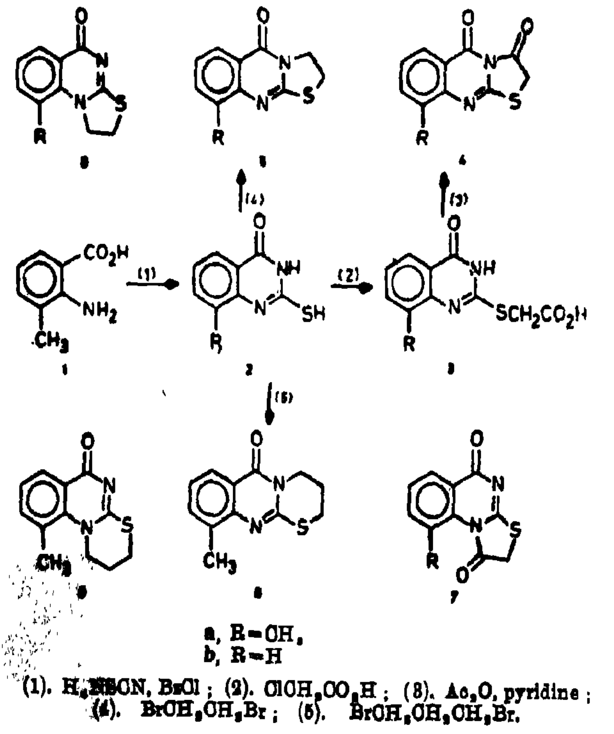
Heterocyclic Systems Containing Bridgehead Nitrogen Atom. Part—XLVII. Syntheses of Thiazolo[2,3-*b*]quinazoline and Thiazino[2,3-*b*]quinazoline

G. D. GUPTA and H. K. PUJARI*

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

2-Mercapto-8-methyl-3,4-dihydroquinazolin-4-one (2a), obtained by the reaction of 3-methylanthranilic acid (1) with ammonium thiocyanate, on condensation with chloroacetic acid gives the acid (3a) which on treatment with acetic anhydride and pyridine undergoes cyclodehydration to furnish a single product to which 9-methyl-2*H*-thiazolo [2,3-*b*]quinazolin-3,5-dione (4a) and not 5-methyl-2*H*-thiazolo[3,2-*a*]quinazolin-3,9-dione (7a) was assigned on the basis of pmr spectral data. Similarly, (2a) on condensation with 1,2-dibromoethane and 1,3-dibromopropane yields 2,3-dihydro-9-methylthiazolo [2,3-*b*]quinazolin-5-one (5a) and 4*H*-2,3-dihydro-10-methyl[1,3]thiazino[2,3-*b*]quinazolin-6-one (6), respectively.

KENDALL and Duffin[1] reported in a British patent that the cyclisation of 3,4-dihydroquinazolin-4-one-2-thiolacetic acid (**3b**), obtained by the reaction of 2-mercapto-3,4-dihydroquinazolin-4-one (**2b**) with chloroacetic acid, yielded a cyclised product which may be represented by either 2*H*-thiazolo [2,3-*b*]quinazolin-3,5-dione (**4b**) or 2*H*-thiazolo[3, 2-*a*]quinazolin-3,9-dione (**7b**). They, however, did not characterise the cyclised product. Dhatt and Narang[2] repeated the above work and found that the acid (**3a**) on heating with acetic anhydride and pyridine underwent decomposition.



a, R = CH_3, **b**, R = H

(1). H_4NSCN, HCl; (2). $ClCH_2CO_2H$; (3). Ac_2O, pyridine; (4). $BrCH_2CH_2Br$; (5). $BrCH_2CH_2CH_2Br$.

2-Mercapto-8-methyl-3,4-dihydroquinazolin-4-one (**2a**), prepared by the condensation of 3-methylanthranilic acid (**1**) with ammonium thiocyanate following the method of Frank and Smith[3] for the synthesis of phenylthiourea, when reacted with chloroacetic acid gave 8-methyl-3,4-dihydroquinazolin-4-one-2-thiolacetic acid (**3a**). The acid (**3a**), being unsymmetrical, on cyclisation was expected to give 9-methyl-2*H*-thiazolo[2, 3-*b*]quinazolin-3, 5-dione (**4a**) or 5-methyl-2*H*-thiazolo[3,2-*a*]quinazolin-3,9-dione (**7a**) or both depending upon the mode of cyclisation. The acid (**3a**), however, on treatment with acetic anhydride underwent cyclodehydration furnishing a single product (tlc). The absorption of carbonyl groups at 1680 and 1775 cm^{-1} in the ir spectrum of the cyclised product though supported the cyclic nature of the product yet could not decide firmly the presence or absence of –CO–N–CO group[4]. The molecular ion peak (M^+) at *m/z* 232 exhibited in the mass spectrum of the tlc-pure product supported the molecular formula, thus corroborating the cyclisation product. However, the structure, 9-methyl-2*H*-thiazolo[2,3-*b*]quinazolin-3,5-dione (**4a**) was finally assigned to this cyclisation product in preference to the structure, 5-methyl-2*H*-thiazolo[3,2-*a*]quinazolin-3,9-dione (**7a**) on the basis of pmr spectral studies.

The reaction of 2-mercapto-8-methyl-3,4-dihydroquinazolin-4-one (**2a**) with 1,2-dibromoethane also gave a tlc-pure single product which could be represented either by the structure 9-methyl-2,3-dihydrothiazolo[2,3-*b*]quinazolin-5-one (**5a**) or 5-methyl-2,3-dihydrothiazolo[3,2-*a*]quinazolin-9-one (**8a**). The exhibition of the molecular ion peak (M^+) at *m/z* 218 in the mass spectrum of this tlc-pure product supports the cyclisation product **5a** or **8a**. In either structure, the signal at δ 2.18 was assignable to methyl protons. The appearance of methyl signal at δ 2.20 (which is almost of the same

value as 2.18) in the pmr spectrum of the cyclisation product obtained from **3a** led to the assignment of the structure **4a** for the cyclisation product. Where the structure **7a** correct, then the methyl protons would have shown a downfield shift due to the deshielding effect of carbonyl group of thiazolidionone ring. The magnetic anisotropic effect of a similar carbonyl group has been found to deshield the *peri*-methyl protons[5] to an appreciable extent.

Howard and Klein[6] obtained 2,3-dihydrothiazolo[2,3-*b*]quinazolin-5-one (**5b**) by the reaction of **2b** with 1,2-dibromoethane, while the reaction of ethyl-*N*-thiocarbamoylanthranilate with 1,2-dibromoethane yielded 2,3-dihydrothiazolo[3,2-*a*]quinazolin-9-one (**8b**) although structure **5b** was assigned to this product earlier by Narang *et al*[7]. The structure **5** was assigned to the tlc-pure cyclisation product obtained from the reaction of **2b** with 1,2-dibromoethane on the analogy with the structure **4** as well as the work of Howard and Klein[6].

Similarly, the reaction of **2a** with 1,3-dibromopropane gave a tlc-pure single product to which the structure 10-methyl-4*H*-2,3-dihydro[1,3]thiazino[2,3-*b*]quinazolin-6-one (**6**) and not **9** was assigned on analogy with the structure **4a** although the pmr data (*vide* experimental) and the exhibition of molecular ion peak (M^+) at *m/z* 232 corroborate the cyclisation product.

Fungicidal test : For fungicidal assay, the method of Aytoun *et al.*[8] was used. *Aspergillus flavus*, *Candida albicans*, *Microsporum gypseum* and *Nocardia asteroidis* were used as test fungi. The thiazolidinone (**4a**) was found to be active against all the fungi at 1 : 500 dilution.

Bactericidal test : The Riedel-Walker[9] serial drop dilution method was used for comparative antibacterial activity using 24 h old culture of *Staphylococcus aureus* and *Escherichia coli*. Here also only the thiazolidinone was found to be active against both the bacteria at 1 : 500 dilution.

Experimental

Melting points reported are uncorrected. Tlc was performed on silica gel plates using acetone-benzene (1 : 3) as the solvent system. Ir spectra (nujol) were recorded on a Beckman IR-20 spectrophotometer. Pmr spectra were run on Perkin-Elmer 90 MHz spectrometer using TMS as the internal reference. Mass spectra were scanned on Hitachi RMU-6 spectrometer.

3-Methylanthranilic acid (**1**) : It was prepared in 60% yield from 7-methylisatin following the method of Baker *et al.*[10] for the synthesis of 3-chloroanthranilic acid, m.p. 172° (lit.[11] 172).

8-Methyl-2-mercapto-3,4-dihydroquinazolin-4-one (**2a**) : 3-Methylanthranilic acid (**1** ; 7.55 g, 0.05 mol) was heated with ammoniumthiocyanate (4.56 g, 0.06 mol) following Frank and Smith[8] synthesis for phenylthiourea to give 8-methyl-2-mercapto-3,4-dihydroquinazolin-4-one (55%), m.p. 262° (aq. DMF) (Found : S, 16.52 ; N, 14.26. $C_9H_8N_2SO$ requires S, 16.67 ; N, 14.58%) ; ν_{max} 1150 (C=S), 1550 (C–N), 1610 (C=N), 1675 (C=O), 3100 cm^{-1} (N–H).

8-Methyl-3,4-dihydroquinazolin-4-one-2-thiolacetic acid (**3a**) : 8-Methyl-2-mercapto-3,4-dihydroquinazolin-4-one (**2a** ; 1.92 g, 0.01 mol) in DMF–NaOH (1.5 g of NaOH in a mixture of 15 ml DMF and 10 ml of water) was added to a mixture of chloroacetic acid (2.88 g, 0.03 mol) in sodium carbonate solution (3.0 g of Na_2CO_3 dissolved in a mixture of 10 ml DMF and 15 ml water) and the reaction mixture was heated on steam bath for 3 h. The suspended impurities were removed by filtration, the filtrate poured into water (50 ml) and then acidified with concentrated hydrochloric acid. The white solid, thus separated, was filtered, washed well with water and crystallised from ethanol as white flakes (1.7 g, 68%), m.p. 240° (d) (Found : S, 13.20 ; N, 11.34. $C_{11}H_{10}N_2SO_3$ requires S, 12.80 ; N, 11.20%) ; ν_{max} 1600, 1635 (C=N and C=C), 1690 (C=O), 2580-2700 cm^{-1} (COOH).

9-Methyl-2H-thiazolo[2,3-b]quinazolin-3,5-dione (**4a**) : A mixture of **3a** (1.0 g), acetic anhydride (1 ml) and pyridine (3 ml) was heated on a steam bath for 20 min. The reaction mixture was cooled and poured into water. The solid, thus obtained, was filtered, washed thoroughly with water and finally crystallised from aq. DMF as light brown flakes (0.4 g, 43%), m.p. 212° (Found : S,13.92 ; N, 11.92, M^+ at *m/z* 232. $C_{11}H_8N_2SO_2$ requires S, 13.79 ; N, 12.07%, mol.wt. 232) ; ν_{max} 1590 (C=N), 1680, 1775 cm^{-1} (both carbonyl groups in O=C–N–C=O) ; δ(TFA) 2.20 (3H, s, CH_3), 4.06 (2H, s, CH_2) 7.08-7.82 (3H, m, Ar-H).

9-Methyl-2,3-dihydrothiazolo[2,3-b]quinazolin-5-one (**5a**) : A solution of 8-methyl-2-mercapto-3,4-dihydroquinazolin-4-one (**2a** ; 0.96 g, 0.005 mol) in 60% aq. isopropanol (25 ml) containing sodium hydroxide (0.2 g) and sodium carbonate (1.75 g) was added in small lots to a refluxing solution of 1,2-dibromoethane (2 ml in 10 ml of isopropanol) and refluxing was continued for 4 h. Isopropanol was distilled off and the solid, thus obtained, was filtered, washed well with water and finally crystallised from ethanol giving cream coloured needles (0.70 g, 64%), m.p. 164-65° (Found : S, 14.35 ; N, 12.52, M^+ at *m/z* 218, $C_{11}H_{10}N_2SO$ requires S, 14,68 ; N, 12.84%, mol. wt. 218) ; ν_{max} 1580, 1600 (C=C and C=N), 1675 cm^{-1} (C=O) ; δ (TFA) 2.18 (3H, s, CH_3), 3.49 (2H, t, SCH_2), 4.46 (2H, t, NCH_2), 7.07-7.77 (3H, m, Ar-H).

10-Methyl-4H-2,3-dihydro[1,3]thiazino[2,3-b]quinazolin-6-one (**6a**) : To a refluxing solution of 1,3-dibromopropane (2 ml in 10 ml isopropanol) was added in small lots, a solution of 8-methyl-2-mercapto-3,4-dihydroquinazolin-4-one (**2a** ; 0.96 g, 0.005 mol) in 60% aqueous isopropanol (25 ml) containing sodium hydroxide (0.2 g) and sodium bicarbonate (1.75 g) and refluxing continued for 4 h. Isoproapanol was distilled off and the aqueous

solution left behind was allowed to stand overnight. The solid, thus obtained, was filtered, washed thoroughly with water and finally crystallised from ethanol to give 10-methyl-4*H*-2,3-dihydro[1,3]thiazino[2,3-*b*]quinazolin-6-one as light brown needles (0.6 g, 52%), m.p. 135° (Found : S, 13.62 ; N, 12.24, M^+ at *m/z* 232. $C_{12}H_{12}N_2SO$ requires S, 13.79 ; N, 12.07%, mol. wt. 232) ; ν_{max} 1540 (C–N stretching), 1590, 1610 (C=N and C=C), 1670 cm^{-1} (C=O) ; δ (TFA) 2.33-2.69 (5H, m, CH_3 and $SCH_2CH_2CH_2N$), 3.48 (2H, t, SCH_2), 4.36 (2H, t, NCH_2), 7.48-7.83 (2H, m, H_8 and H_9) and 8.18 (1H, d, each broad, H_7, $J_{7,8}$ 8 Hz).

Acknowledgement

The authors wish to express their sincere thanks to Prof. L. N. Mohapatra, Head of the Department of Microbiology, A.I.I.M.S., New Delhi for biological screening. One of the authors (G.D.G.), thanks U.G.C., New Delhi for the award of a Teacher Fellowship and the Government of Haryana for the grant of Academic Leave.

References

1. J. D. KENDALL and G. F. DUFFIN, *Brit. Pat.* 634. 951 (*Chem. Abstr.*, 1950, **44**, 9287).
2. M. S. DHATT and K. S. NARANG, *J. Indian Chem. Soc.*, 1954, **31**, 787.
3. R. L. FRANK and P. V. SMITH, *Org. Synth.*, 1953, **3**, 735.
4. S. C. BELL and G. CONKLIN, *J. Heterocycl. Chem.*, 1968, **5**, 179.
5. H. S. CHAUDHARY, C. S. PANDA and H. K. PUJARI, *Indian J. Chem.*, 1970, **8**, 10.
6. J. C. HOWARD and G. KLEIN, *J. Org. Chem.*, 1962, **27**, 3701.
7. K. S. NARANG, M. C. KHOSLA, O. P. VIG and I. S. GUPTA, *J. Sci. Ind. Res., Sect. B*, 1953, **12**, 446.
8. R. S. C. AYTOUN, A. H. CAMPBELL, E. J. NAPIER and D. A. L. SCILER, *Arch. Derm.* 1960, **81**, 650.
9. S. RIDEAL and J. F. A. WALKER, *J. Roy. Sanit. Inst.*, 1903, **24**, 424.
10. B. R. BAKER, R. E. SCHAUB, J. P. JOSEPH, F. J. MCEVOY and J. H. WILLIAMS, *J. Org. Chem.*, 1952, **17**, 143.
11. I. HEILBRON and H. M. BUNBURY, "Dictionary of Organic Compounds", Eyre and Spottiswoode, London, 1953, Vol. I, p. 143.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1053-1056

Reaction of 2-Mercapto-4-chloro-6-bromobenzimidazole with Chloroacetic acid, α-Halogenoketones and Alkyl Bromides

(Miss) KIRAN JAIN, K. K. JAIN, V. K. CHADHA** and R. N. HANDA*

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

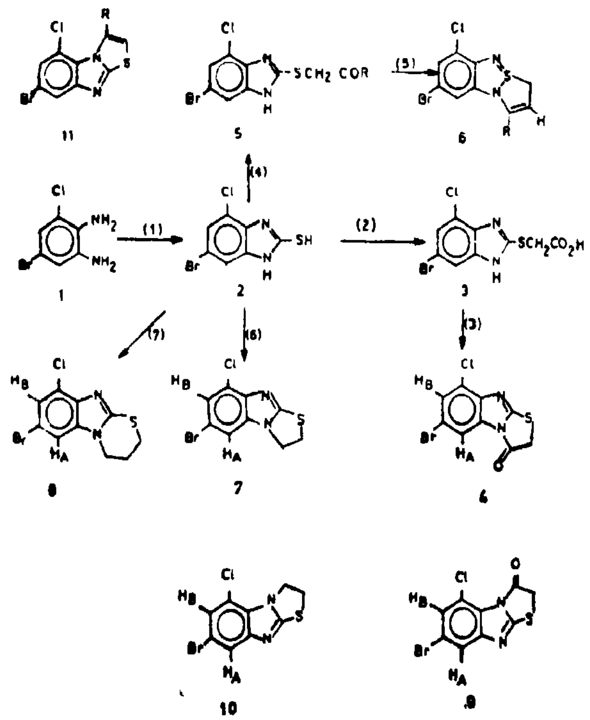
The syntheses of 6-bromo-8 chlorothiazolo[3,2-*a*]benzimidazol-3(2*H*)-one (4), 3-aryl-6-bromo-8-chlorothiazolo[3,2-*a*]benzimidazoles (6), 2,3-dihydro-6-bromo-8-chlorothiazolo[3,2-*a*]benzimidazole (7) and 4*H*-2,3-dihydro-7-bromo-9-chloro[1,3]thiazino-[3,2-*a*]benzimidazole (8) have been achieved starting from 2-mercapto-4-chloro-6-bromobenzimidazole (2). Compound 2, obtained by the reaction of 4-bromo-6-chloro-1,2-diaminobenzene (1) with carbon disulphide, on condensation with chloroacetic acid gives the acid 3, which on cyclisation with acetic anhydride furnishes 4, and not the other isomer 9 as revealed by pmr spectral data. Condensation of 2 with α-halogenoketones followed by PPA cyclisation of the intermediate ketone (5) yields 6. Similarly, the reaction of 2 with 1,2-dibromoethane and 1,3-dibromopropane gives 2,3-dihydro-6-bromo-8-chlorothiazolo[3,2-*a*]benzimidazole (7) and 4*H*-2,3-dihydro-7-bromo-9-chloro[1,3]thiazino [3,2-*a*]benzimidazole (8), respectively.

THE syntheses of 6-bromo-8-chlorothiazolo[3,2-*a*]benzimidazol-3(2*H*)-one (**4**), 3-aryl-6-bromo-8-chlorothiazolo[3,2-*a*]benzimidazoles (**6**), 2,3-dihydro-6-bromo-8-chlorothiazolo[3,2-*a*]benzimidazole (**7**) and 4*H*-2,3-dihydro-7-bromo-9-chloro[1,3]thiazino [3,2-*a*]benzimidazole (**8**) reported in the present communication, were undertaken to study the directive influence of bromine and chlorine atoms on cyclisation of their precursors. 2-Mercapto-4-chloro-6-bromobenzimidazole (**2**) obtained by the treatment of 3-chloro-5-bromo-1,2-diaminobenzene (**1**) with carbon disulphide, when condensed with chloroacetic acid gave 4-chloro-6-bromobenzimidazol-2-thiolacetic acid (**3**). The acid (**3**), being unsymmetrical is expected to give 6-bromo-8-chlorothiazolo[3,2-*a*]benzimidazol-3(2*H*)-one (**4**), or 5-chloro-7-bromothiazolo[3,2-*a*]benzimidazol-3(2*H*)-one (**9**) or both depending upon the direction of cyclisation. The acid (**3**), however, when heated in a mixture of acetic anhydride and pyridine underwent cyclisation furnishing a single product (tlc). The appearance of a band at 1735 cm^{-1} (N – C = O) in the ir spectrum of the tlc-pure product confirmed the cyclisation. Further confirmation that the cyclisation did occur comes from the mass spectrum of this compound which showed the isotopic cluster of molecular ion peaks at *m*/*z* 302 (P), 304 (P+2) and 306 (P+4) indicating the presence of one atom of bromine and one atom of chlorine and supports the moleculer formula. The structure **4** has been finally assigned to this tlc-pure product on the basis of pmr spectral data in preference to **9**.

The reaction of 2-mercapto-4-chloro-6-bromobenzimidazole (**2**) with 1,2-dibromoethane gave a single product (tlc) which could be represented either by structure **7** or **10**. In either of the structure the signals at 7.71 and 7.77 may be due to H_A and H_B (not necessarily), respectively It may be noted that H_A and H_B resonate in close proximity, the difference between the two signals (7.77-7.71) is 0.06 Hz. In structure **9**, both the aromatic protons (H_A and H_B) will resonate in close proximity to each other as observed in **7** (or **10**), whereas in **4**, H_A will be deshielded by the thiazolidinone ring and as a result H_A will resonate at downfield in respect to the other proton, H_B. The deshielding has its origin in the magnetic anisotropy of the carbonyl group with minor contribution from the rest of the thiazolidinone ring. Comparison of the chemical shifts of H_A in **7** (or **10**) having a value at δ 7.71 (or 7.77) and the signal at δ 8.24 (a value sufficiently higher than 7.71 or 7.77, and is due to the deshielding effect of the carbonyl group) exhibited by the cyclised product obtained from the acid (**3**) supports the structure **4**. Such a downfield shift would not be expected from the structure **9**. The other proton H_B resonate at δ 7.84 and the difference in chemical shifts of H_A and H_B (8.24-7.84) is 0.40 Hz. The magnetic anisotropic effect of similar carbonyl group has been found to deshield the *peri*-protons[1,2] to an appreciable extent. After having established the structure **4**, the structure **7** (and not **10**) for the product obtained from the reaction of **2** with 1,2-dibromoethane was assigned on analogy with structure **4**. The exhibition of isotopic cluster of molecular ion peaks at *m*/*z* 288 (P), 290 (P+2) and 292 (P+4) indicating the presence of one bromine and one chlorine atoms supports the molecular formula.

** Department of Biochemistry, College of Medicine, University of Iowa, Iowa City, Iowa 52242, U.S.A.

2-Mercapto-4-chloro-6-bromobenzimidazole (2) on condensation with α-halogenoketones yielded ketones (5) (ν_{max} 1655-1670 cm^{-1}, C=O) which on treatment with PPA underwent cyclisation giving a single compound (tlc) in each case. Ir (absence of carbonyl band) and pmr (one proton singlets at δ 7.36 and 7.26 due to C_8-H exhibited by the cyclized product obtained from 5 ($R=C_6H_5$) and 5 ($R=p-H_3C-C_6H_4$), respectively) spectra confirmed the tlc-pure product to have a cyclic structure. The cyclisation had indeed occurred was further confirmed by mass spectral data. The exhibition of isotopic cluster of molecular ion peaks at *m/z* 362 (P), 364 (P+2) and 366 (P+4) and 376 (P), 378 (P+2) and 380 (P+4) in the mass spectra of the compounds obtained from the cyclisation of 5 ($R=C_6H_5$) and 5 ($R=p-H_3C-C_6H_4$), respectively indicates the presence of one bromine and one chlorine atoms and supports the molecular formulae. But the pmr and mass spectral data were not of much help in deciding in favour of either structure 6 or 11, the formation of which are possible during the cyclisation of ketone 5, because of its unsymmetrical nature. Assignment of structure 6 was, however, based on analogy with the strcture 4.



(1) CS_2, KOH ; (2) $ClCH_2CO_2H$, NaOAc ; (3) Ac_2O, pyridine ; (4) $RCOCH_2Br$; (5) PPA ; (6) $BrCH_2CH_2Br$; (7) $BrCH_2CH_2CH_2Br$.

Similarly, 2-mercapto-4-chloro-6-bromobenzimidazole (2) on reaction with 1,3-dibromopropane furnished a tlc-single product to which structure 4*H*-2,3-dihydro-7-bromo-9-chloro[1,3]thiazino[3,2-*a*]benzimidazole (8) has been assigned on the analogy with structure 4. Here also the appearance of one multiplet centred at δ 2.67 integrated for two protons ($-SCH_2CH_2CH_2N-$), two triplets, at 3.48 and 4.93 each integrated for two protons (SCH_2 and NCH_2, respectively) two doublets each integrated for one proton at 7.68 and 7.73 (aromatic protons H_A and H_B not necessarily, respectively) in the pmr spectrum of the product obtained from the reaction of 2 with 1,3-dibromopropane, suggests that the cyclisation had indeed occurred, although the pmr spectral data were not of much help in deciding the location of bromine and chlorine atoms in the tlc-pure product.

Fungicidal tests: For fungicidal assay, the method of Aytoun *et al.*[3] was used. *Aspergillus flavus*, *Candida albicans*, *Microsporum gypseum* and *Nocardia asteroides* were used as test fungi. Among the compounds screened, compound 4 and 6 ($R=p-H_3C-C_6H_4$) were found to possess activity against *Candida albicans* and *Nocardia asteroides* at 1 : 500 dilution ; 7 against *Candida albicans*, *Microsporum gypseum* and *Nocardia asteroides* at 1 : 500 dilution.

Antibacterial tests: For antibacterial test, the Rideal-Walker[4] serial drop dilution method was used. The test organisms were 24 h old culture of *Staphylococcus aureus* and *Escherichia coli*. Compounds 4, 6 ($R=p-H_3C-C_6H_4$) and 7 were found to possess activity against *S. aureus* and *E. coli* at 1 : 500 dilution.

Experimental

All melting points are uncorrected. Tlc was performed on silica gel plates using acetone-benzene (1 : 3) as the solvent system. Ir spectra (nujol) were recorded on a Beckman IR-20 spectrophotometer. Pmr spectra were run on a Perkin-Elmer 90 MHz spectrometer using TMS as the internal reference standard. Mass spectra were scanned on Hitachi RMU-6 spectrometer.

3-Chloro-5-bromo-1,2-diaminobenzene (1) : 2-Chloro-4-bromoacetanilide obtained from *o*-chloroaniline by acetylation and subsequent bromination, on nitration followed by hydrolysis yielded 2-chloro-4-bromo-6-nitroaniline, m.p. 117° (lit[5]. 117-18°). The nitroaniline on reduction with Raney nickel and hydrazine hydrate, following the usual procedure furnished the desired diamine (1) which was immediately used for the preparation of mercaptobenzimidazole (2).

2-Mercapto-4-chloro-6-bromobenzimidazole (2) : It was synthesised in 60% yield by the reaction of 3-chloro-5-bromo-1,2-diaminobenzene (1) with carbon disulphide following the method of Van Allan and Deacon[6] for the synthesis of 2-mercaptobenzimidazole, m. p. >300° (EtOH-DMF) (Found : S, 12.22 ; N, 11.09. $C_7H_4N_2BrClS$ requires S, 12.14 ; N, 10.62%) ; ν_{max} 1180, 1195 (C=S), 1600 (C=N), 3040 and 3420 cm^{-1} (N-H).

4-Chloro-6-bromobenzimidazo-2-thiolacetic acid (**3**) : A mixture of 2-mercapto-4-chloro-6-bromobenzimidazole (**2** ; 2.63 g, 0.01 mol), chloroacetic acid (0.96 g, 0.01 mol) and potassium hydroxide (0.56 g, 0.01 mol) in ethanol (100 ml) was heated, under reflux, for 3 h. The reaction mixture was cooled to room temperature, acidified with dilute acetic acid and kept overnight. The white solid, thus separated, was filtered and washed with water. Crystallisation from ethanol furnished white needles (2.0 g, 62%), m.p. 221° (Found : S, 10.32 ; N, 8.94. $C_9H_6N_2BrClSO_2$ requires S, 9.95 ; N, 8.70%) ; ν_{max} 1610 (C=N), 2660-2700 (COOH) and 3070 cm^{-1} (N–H bonded).

6-Bromo-8-chlorothiazolo[3,2-a]benzimidazol-3(2H)-one (**4**) : 4-Chloro-6-bromobenzimidazo-2-thiolacetic acid (**3** ; 1.0 g) in a mixture of acetic anhydride (1.0 ml) and pyridine (3.0 ml) was heated on a steam bath for 15 min. The reaction mixture was kept overnight and the solid, thus separated, was filtered, washed with water and finally crystallised from ethanol as white flakes (0.5 g, 53%), m.p. 251° (Found : S, 10.83 ; N, 9.62 ; M^+ at m/z 302, 304 and 306 showing the presence of one bromine and one chlorine atoms. $C_9H_4N_2BrClSO$ requires S, 10.54 ; N, 9.22% ; mol. wt. 303.5) ; ν_{max} 1500 (C–N), 1570, 1605 (C=N) and 1735 cm^{-1} (C=O) ; δ (TFA–$CDCl_3$) 4.75 (2H, s, CH_2), 7.84 (1H, d, H_B, J_{AB} 2Hz), 8.24 (1H, d, H_A, J_{AB} 2Hz).

2-p-Methylphenacylthio-4-chloro-6-bromobenzimidazole (**5**, R=p-$H_3C-C_6H_4$) : A mixture of 4-chloro-6-bromo-2-mercaptobenzimidazole (**2** ; 1.315 g, 0.005 mol) and p-methylphenacyl bromide (1.665 g, 0.005 mol) in anhydrous ethanol (30 ml) and DMF (30 ml) was heated, under reflux, for 6 h. The reaction mixture was cooled to room temperature and the hydrobromide, thus separated, was neutralised with sodium carbonate. The free base, so obtained, was filtered, washed with water and crystallised from ethanol to furnish pale yellow needles, (1.2 g, 60%), m.p. 280° (Found : S, 8.42 ; N, 7.47. $C_{16}H_{12}N_2ClBrSO$ requires S, 8.09 ; N, 7.07%) ; ν_{max} 1600 (C=N), 1665 (C=O) and 3320 cm^{-1} (N–H).

Similarly, **5** (R=C_6H_5), m.p. 220° (Found : S, 8.63 ; N, 7.60. $C_{15}H_{10}N_2BrClSO$ requires S, 8.39 ; N, 7.34%) ; ν_{max} 1590 (C=N), 1670 (C=O) and 3260 cm^{-1} (N–H) was prepared in 52% yield.

3-p-Tolyl-6-bromo-8-chlorothiazolo[3,2-a]benzimidazole (**6**, R=p-$H_3C-C_6H_4$) : A mixture of 2-p-methylphenacylthio-4-chloro-6-bromobenzimidazole (**5**, R=p-$H_3C-C_6H_4$; 1.0 g,) phosphorus pentoxide (4.0 g) and orthophosphoric acid (3.0 ml) was heated on an oil bath at 150-60° for 3 h. The reaction mixture was cooled to room temperature, poured into ice-cold water and neutralised with sodium carbonate. The solid, so obtained, was filtered, washed with water and crystallised from ethanol as light brown needles (0.5 g, 52%), m.p. 255° (Found : S, 8.25 ; N, 7.83 ; M^+ at m/z 376, 378 and 380 showing the presence of one bromine and one chlorine atoms. $C_{16}H_{10}N_2BrClS$ requires S, 8.47 ; N, 7.41% ; mol. wt. 377.5) ; ν_{max} 1550 (C–N stretching) and 1600 cm^{-1} (C=N, C=C) ; δ (TFA–$CDCl_3$) 2.58 (3H, s, CH_3), 7.26 (1H, s, C_2–H) and 7.40-7.84 (6H, m, Ar–H).

Similarly, **6** (R=C_6H_5), m.p. >300° (Found : S, 8.72 ; N, 7.31 ; M^+ at m/z 362, 364 and 366 showing the presence of one bromine and one chlorine atoms. $C_{15}H_8N_2BrClS$ requires S, 8.80 ; N, 7.70% ; mol. wt. 363.5) ; ν_{max} 1515 (C–N) and 1605 cm^{-1} (C=N and C=C) ; δ (TFA–$CDCl_3$) 7.36 (1H, s, C_2–H), 7.64-7.88 (7H, m, Ar–H), was prepared in 42% yield.

2,3-Dihydro-6-bromo-8-chlorothiazolo[3,2-a]benzimidazole (**7**) : A mixture of 2-mercapto-4-chloro-6-bromobenzimidazole (**2** ; 1.315 g, 0.005 mol) and 1, 2-dibromoethane (0.94 g, 0.005 mol) in anhydrous ethanol (30 ml) was refluxed for 6 h. The reaction mixture was cooled to room temperature and poured into ice-cold water and basified with sodium carbonate. The free base, thus obtained, was filtered, washed with water and crystallised from ethanol giving light brown needles (0.8 g, 53%), m.p. 170° (Found : S, 11.41 ; N, 10.29 ; M^+ at m/z 288, 290 and 292 showing the presence of one bromine and one chlorine atoms. $C_9H_6N_2BrClS$ requires S, 11.05 ; N, 9.66% ; mol. wt. 289.5) ; ν_{max} 1560 and 1605 cm^{-1} (C=N) ; δ(TFA–$CDCl_3$) 4.34 (2H, t SCH_2), 5.06 (2H, t, NCH_2), 7.71 (1H, d, H_A or H_B J_{AB} 2.0 Hz) and 7.77 (1H, d, H_B or H_A, J_{AB} 2.0 Hz).

4H-2,3-dihydro-7-bromo-9-chloro[1,3] thiazino[3,2-a]benzimidazole (**8**) : A mixture of **2** (1.315 g, 0.05 mol) and 1,3-dibromopropane (1.01 g, 0.005 mol), anhydrous ethanol (30 ml) and DMF (30 ml) was heated, under reflux, for 5 h. The reaction mixture was poured into cold water and neutralised with ammonium hydroxide. The solid, thus obtained, was filtered, washed with water and crystallised from ethanol as white crystals (0.7 g, 46%), m.p. 155-56° (Found : S, 10.15 ; N, 9.30. $C_{10}H_8N_2BrClS$ requires S, 10.54 ; N. 9.22%) ; ν_{max} 1565 (C–N stretching) and 1600 cm^{-1} (C=N) ; δ(TFA–$CDCl_3$) centred at 2.67 (2H, m, $SCH_2CH_2CH_2N$), 3.48 (2H, t, SCH_2), 4.93 (2H, t, NCH_2), 7.68 (1H, d, H_A or H_B, J_{AB} 2 Hz) and 7.73(1H, d, H_B or H_A, J_{AB} 2 Hz).

Acknowledgement

The authors wish to express their sincere thanks to Prof. L. N. Mohapatra, Head of the Department of Microbiology, A.I.I.M.S., New Delhi for biological screening. One of the authors (K.K.J.) is grateful to U.G.C., New Delhi for a Teacher Fellowship and to the authorities of G.M.N. College, Ambala Cantt for grant of leave and the other (K.J.) is grateful to the C.S.I.R., New Delhi for the award of Junior Research Fellowship.

References

1. E. C. TAYLOR and A. MCKALLOP, *J. Am. Chem. Soc.*, 1965, **87**, 1984.
2. R. H. MARTIN, N. DEFAY and F. GEERTS-EVRARD, *Tetrahedron*, 1964, **20**, 1505.
3. R. S. C. AYTOUN, A. H. CAMPBELL, E. J. NAPIER and D. A. L. SCILER, *Arch. Derm.*, 1961, **81**, 650.
4. S. BIDEAL and J. F. A. WALKER, *J. Roy. Sanit. Inst.*, 1903, **24**, 424.
5. N. G. CLARK and A. F. HANS, *J. Sci. Food Agric.*, 1961, **12**, 751 (*Chem. Abstr.*, 1962, **56**, 7746).
6. J. A. VAN ALLAN and B. D. DEACON, *Org. Synth.*, 1963, **4**, 569.

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984, pp. 1057-1060

Protease Activity of Rabbit Brain Tissue

MOHAN LAL, (Miss) KAMLESH MIGLANI and HARI SINGH*

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

The complete spectrum of protease activity of rabbit brain homogenate was not revealed by traditional protease substrates, haemoglobin and casein. Whereas, these two substrates sufficed for detecting protease activity at acidic and alkaline *p*Hs, azocasein, a chromogenic substrate was needed to demonstrate an important protease activity peak at slightly acidic *p*H values. The brain homogenate contains protease activity over the entire *p*H range from 2.0-10.0 with peaks of activity around *p*H 3.5, 5.0 and 8.5. Pepstatin, a specific inhibitor of cathepsin D was utilised to show that almost entire protease activity in peak I was due to this protease. That the second peak consisted of cathepsin B and BANA-hydrolase was shown by using BANA as substrate and leupeptin as inhibitor. Leupeptin, a specific inhibitor for cathepsin B could not completely abolish the BANA-hydrolase activity at 1.0 μM concentration sufficient to completely inhibit the activity of pure cathepsin B. Further, Z-L-Arg-L-Arg-4mβNA, a highly specific chromogenic substrate for cathepsin B was utilised for the first time to demonstrate the presence of cathepsin B in rabbit brain. At 1.0 μM concentration of leupeptin, the complete inhibition of Z-Arg-Arg-4mβNA activity confirms the presence of cathepsin B.

SMALL bio-active peptides are present in the central nervous system. They act as neurotransmitters and regulators of hormonal activity. The control mechanism for these neuropeptides, *i.e.* their formation and inactivation has generated tremendous interest in the field of neurochemistry but evaded proper understanding as yet. In a recent review, Marks[1] has highlighted the involvement of brain proteases *vis-à-vis* these biopeptides. Most of the work in the area of brain proteases has been done on acid-acting hydrolase[1-4], cathepsin D (EC 3.4. 23.5) and some neutral and alkaline proteases[1,5,6]. In our overall programme of identifying peptide hydrolases present in the central nervous system, we had reported earlier[7] that the brain tissue contains proteases active over the entire *p*H range from 2.5 to 10.5. The most prominent peak was, however, at *p*H 3.5-4.0 which was shown by the use of a specific inhibitor pepstatin, to be entirely due to cathepsin D. In the light of the fact that a very strong peak of activity comprising protein-hydrolyzing enzymes active at slightly acidic *p*H values has been reported from other tissues[8,9], it was thought worthwhile to investigate the presence of such proteinases in brain. In the present study, we report the use of a chromogenic substrate, azocasein, in addition to haemoglobin and casein to detect the proteases active over entire *p*H range. This substrate made possible a new peak of protease activity at slightly acidic *p*H values (not detected by haemoglobin and casein). By using a new and highly specific substrate, Z-Arg-Arg-4mβNA for cathepsin B (EC 3.4.22.1), coupled with its specific inhibitor leupeptin, the presence of cathepsin B and a separate enzyme, BANA-hydrolase is reported.

Experimental

Rabbit brain acetone powder which was used as the source of brain tissue homogenate was purchased from Pel-Freeze Biological Inc. Rogers, (U. S. A.). Haemoglobin, azocasein, dithioerythritol (DTE), α-*N*-benzoyl-D, L-arginine-β-naphthylamide (BANA), bovine serum albumin (BSA), *p*-chloromercuribenzoic acid (PCMB), Fast Garnet GBC dye were purchased from Sigma Chemical Co. (U. S. A.). Leupeptin was procured from Peptide Institute Inc. (Japan). α-*N*-Benzyloxycarbonyl-L-arginine-L-arginine-4-methoxy-β-naphthylamide (Z-Arg-Arg-4mβ-NA) was procured from Enzyme System Products (U.S.A.). All other chemicals used were of highest grade available. Absorption in the uv/visible range was measured on Shimadzu-140-02 (200-1000 nm range) and EC spectrophotometer (350-900 nm range).

Preparation of enzyme homogenate : The rabbit brain acetone powder (10 g) after being stirred for 1 h at 4° in 100 ml of 50 mM sodium acetate buffer *p*H 5.5 containing 0.2 M NaCl, was homogenised thrice for a period of 15 sec each time in an Osterizer blender. Protein estimation was done according to the method of Lowery *et al*[10].

Assay for proteolytic activity : The protease activity of brain homogenate was estimated at various *p*Hs, with haemoglobin, azocasein and casein as substrates. Haemoglobin substrate was prepared by dialysing a 4% aqueous solution of bovine Hb against several changes of ion-free distilled water for 48 h. Azocasein substrate was prepared by dialysing azocasein solution (in 0.1 N NaOH) against water for 48 h. The dialysed azocasein was adjusted to *p*H 6.0 and was made 4%. Casein substrate was prepared by dissolving 4 g casein in 50 mM sodium phosphate buffer, *p*H 7.5. The 4% substrates prepared above were diluted to 1 : 1 with 0.2 M buffers of appropriate *p*Hs for protease assay. 1.0 ml of this resultant 2% substrate in 0.1 M buffer was incubated with 1.0 ml of brain homogenate at 40°

for 3 h. The reaction was stopped by the addition of 3.0 ml of 5% TCA and the precipitated material was filtered off after centrifugation on a table-top centrifuge. Blanks were also prepared where enzyme homogenate was added after the addition of TCA. The activity was measured quantitatively from the filtrate either by measuring absorbance at 280 n*M* or colorimetrically as described earlier[11].

Assay for BANA-hydrolase activity: BANA-hydrolase activity at various *p*Hs was estimated with BANA as substrate: To 1.5 ml of 0.1 *M* buffers of various *p*Hs 0.1 ml each of 40 m*M* EDTA and 40 m*M* DTE were added. After adding 0.2 ml enzyme homogenate, the final *p*Hs of various samples were recorded as, 2.74, 3.45, 4.12, 4.46, 5.07, 5.78, 5.84, 6.2, 6.96, 7.35, 7.8 and 8.7. The reaction was started by the addition of 0.1 ml of BANA stock solution (40 mg/ml in DMSO) and the incubation carried at 40°. After 1 h, the reaction was stopped by the addition of 2.0 ml of coupling reagent. Blanks were included where enzyme was added after the addition of coupling reagent. After allowing 20 min for colour development, the red colour was extracted into 4.0 ml of n-butanol and estimated by measuring absorbance at 520 nm. The activity of BANA hydrolase is expressed in nanomole of β-naphthylamine liberated/h/ml enzyme. The molar extinction coefficient of β-naphthylamine at 520 nm, under the present assay conditions, was taken as 25000[11].

Assay of BANA-hydrolase in presence of leupeptin: Stock solution (0.001*M*) of leupeptin was prepared by dissolving 1.1 mg leupeptin in 2.5 ml incubation buffer (EDTA/phosphate buffer). To 1.498 ml of assay buffers of different *p*Hs (2.45, 2.96, 4.0, 4.85, 5.34, 5.92, 6.54, 6.93, 8.45 and 9.00) 0.2 ml of enzyme was added followed by 2 μl of leupeptin solution in assay buffer to affect a final concentration of 1.0 μM in the assay. After pre-incubation of 10 min, 0.1 ml each of 40 m*M* EDTA and 40 m*M* DTE were added. The final *p*Hs of all the test-tubes were recorded as 2.70, 3.09, 4.02, 4.85, 5.32, 5.77, 6.5, 6.85, 7.62 and 8.1. After further incubation of 5 min, 0.1 ml of BANA stock solution was added to start the reaction. Blanks and control assays were also included, where enzyme was added after the addition of coupling reagent in blanks and no leupeptin was added in control experiments. The reaction products were processed as described above.

Assay of cathepsin B with Z-Arg-Arg-4mβNA as substrate: To 1.0 ml of 0.2 *M* bufferes of various *p*Hs (2.17, 2.96, 4.02, 4.90, 5.53, 6.03, 6.52, 7.49 and 8.42), 0.55 ml water was added followed by 0.2 ml enzyme, 0.1 ml each of 40 m*M* EDTA and 40 m*M* DTE. The reaction was started by the addition of 50 μl of Z-Arg-Arg-4mβNA (8 mg/ml DMSO). The final *p*Hs were recorded as 2.90, 3.26, 4.28, 5.0, 5.62, 6.03, 6.58, 7.27 and 7.68. The reaction tubes were incubated at 40° for 1 h before adding 2.0 ml of coupling reagent. Blanks were also included where enzyme was added after the addition of coupling reagent. Colour was allowed to develop for 20 min after which it was extracted into 4.0 ml of n-butanol and estimated at 520 nm. The unit of activity was expressed in nanomole of 4-methoxy-β-naphthylamine/h/ml enzyme. The molar extinction coefficient of 4-methoxy-β-naphthylamine under present assay conditions was taken as 34900[18].

Assay of cathepsin B with Z-Arg-Arg-4mβNA as substrate in presence of leupeptin: To 1.0 ml of 0.2*M* buffer of various *p*Hs (2.17, 2.96, 4.02, 4.90, 5.53, 6.03, 6.52, 7.49 and 8.42), 0.548 ml of water was added followed by 2 μl of leupeptin, 0.2 ml of enzyme, 0.1 ml each of 40 m*M* DTE and 40 m*M* EDTA, and finally reaction was started by the addition of 50 μl of Z-Arg-Arg-4mβNA (8 mg/ml DMSO). The rest of the procedure was exactly same as described above.

Results and Discussion

Assays for protease activity: Assay procedures had to be standardised[7] due to the large amount of protein present in the crude brain homogenate, capable of influencing the final *p*Hs of the assay mixtures. Accordingly, after mixing the 4% substrate with 0.2*M* buffers of various *p*Hs, the *p*H values were adjusted with 1 *N* HCl or 1 *N* NaOH to yield the 2% substrates of following *p*H values, Hb, 1.43, 2.31, 3.55, 4.78, 5.67, 6.41, 7.03, 7.76, 8.48, 9.29 and 11.58; azocasein, 1.18, 1.46, 3.86, 4.74, 5.22, 6.40, 6.93, 7.15, 8.46, 9.83 and 11.46; and casein, 1.25, 1.72, 3.85, 4.50, 4.97, 5.93, 7.59, 8.59, 9.40, 9.63 and 10.23. When 1.0 ml out of these stock substrate solutions was mixed with 1.0 ml of the enzyme homogenate, the resulting *p*Hs were: Hb, 1.50, 2.51, 3.58, 4.98, 5.80, 6.48, 6.95, 7.52, 8.32, 8.77 and 9.50; azocasein, 2.0, 3.37, 4.41, 5.16, 5.68, 6.65, 7.04, 7.06, 8.32. 9.17 and 10.00; and casein, 1.56, 2.90, 4.08, 4.75, 5.10, 6.25, 7.11, 7.45, 7.89, 8.41 and 9.05. The samples were prepared in quadruplicate so that assays were performed in triplicate and the fourth sample tube was utilised to measure the final *p*H of the assay mixture. The TCA-soluble peptides were quantitated as described above. The azocasein hydrolysing activity was also estimated as absorbance at 366 nm. The activity profiles were the same. Four different experiments done with different enzyme preparations and at different times gave identical results. The results of one typical experiment are shown in Fig. 1. It is abundantly evident that the brain contains proteases active over the entire *p*H range (2.0-10.0). Both the substrates, Hb and casein, which have traditionally been used for measuring the general protease activity show peaks at acid and alkaline *p*H values (peaks, Hb at 3.58 and 8.77; casein at 2.90 atd 8.41). The peaks with Hb and casein are almost overlapping. These results are in agreement with our earlier work[7] where Hb and casein were used over limited *p*H range Hb (2-6), and casein (6-11). The main drawback of using these two substrates becomes

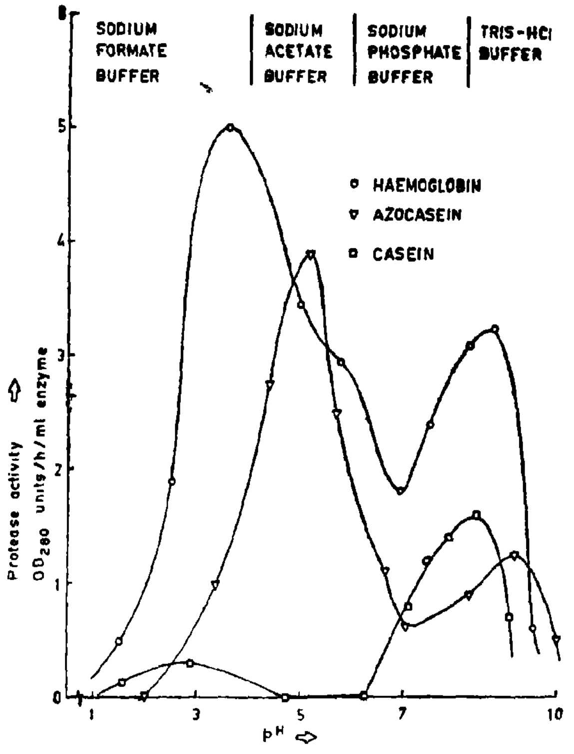


Fig. 1. Protease activity of rabbit brain tissue at different pH values. Buffers used in the pH ranges indicated. Activity expressed as OD_{280} units/h/ml enzyme homogenate at 40° ; haemoglobin (○), azocasein (▽), and casein (□).

apparent from the fact that the proteases which are active at slightly acidic pH values are not detected. When azocasein was used as substrate, a strong peak of activity at pH 5.16 highlights the presence of proteases which are active at slightly acidic pH. Barrett[9] and Singh *et al.*[18] have demonstrated the role of such proteases, present in other tissues, in the degradation of protein substrates.

Identification of proteases present in activity peaks : After demonstrating the presence of proteases in brain tissue active at slightly acidic pH and responsible for the appearance of the third major peak in the activity profile of proteases over the entire pH range, an effort was made to identify the proteases present in the three peaks of Fig. 1. As for the proteases present in first peak (around pH 3.5) we had shown by using a specific inhibitor of cathepsin D that this endopeptidase contributes to a large extent. The inhibitor pepstatin[9] at a final concentration of 0.1 mM abolished ~90% of the activity in peak I[7]. The proteases from rabbit lung[12,18] and rat liver[8,9], which are active at slightly acidic pH and insensitive to pepstatin are cathepsin B, BANA-hydrolase and cathepsin L. The presence of such proteases in central nervous tissue has not yet been reported except for a BANA-hydrolase[14]. When the brain homogenate was scanned for BANA-hydrolysing activity over the entire pH range, maximum activity was obtained between pH 5.5 and 6.0 as shown in Fig. 2. Further characterisation of this BANA-hydrolysing activity was carried out with

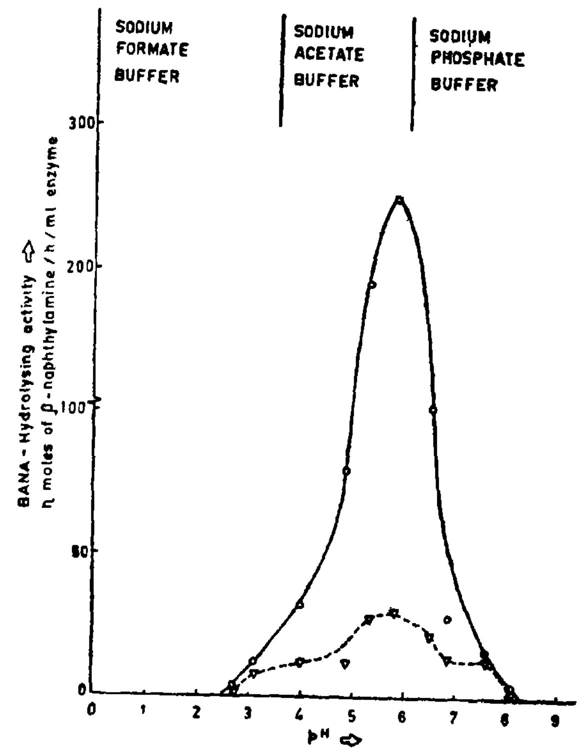


Fig. 2. BANA-hydrolysing activity of rabbit brain tissue at various pH values. Activity expressed as nanomole of β-naphthylamine liberated/h/ml enzyme at 40° : activity without leupeptin (○), and activity with leupeptin (▽).

the help of a specific inhibitor of cathepsin B. This inhibitor, leupeptin[9] (acetyl-L-leucyl-L-leucyl-L-arginal) when incorporated into the assay mixtures at a final concentration of 1 μM, a concentration sufficient for complete inhibition of purified lung cathepsin B[12] did not completely abolish the BANA-hydrolase activity (~85% inhibition). By analogy with the studies on rabbit lung, the leupeptin-insensitive activity may be due entirely to a new enzyme, BANA-hydrolase.

Activity of cathepsin B : The indication for the presence of cathepsin B in brain as detailed above and also mentioned earlier[14] prompted us to utilise for the first time, a new and highly specific chromogenic substrate for cathepsin B, Z-arg-arg-4mβNA[15] to confirm the activity of this protease in brain tissue. The activity profile is shown in Fig. 3. The complete abolition of this activity by the incorporation of 1 μM leupeptin concentration demonstrates beyond doubt the presence of cathepsin B in brain and consequently its contribution in the protease peak II of Fig. 1. The presence of the third protease, cathepsin L has not yet been reported from brain tissue. Experiments are in progress in this

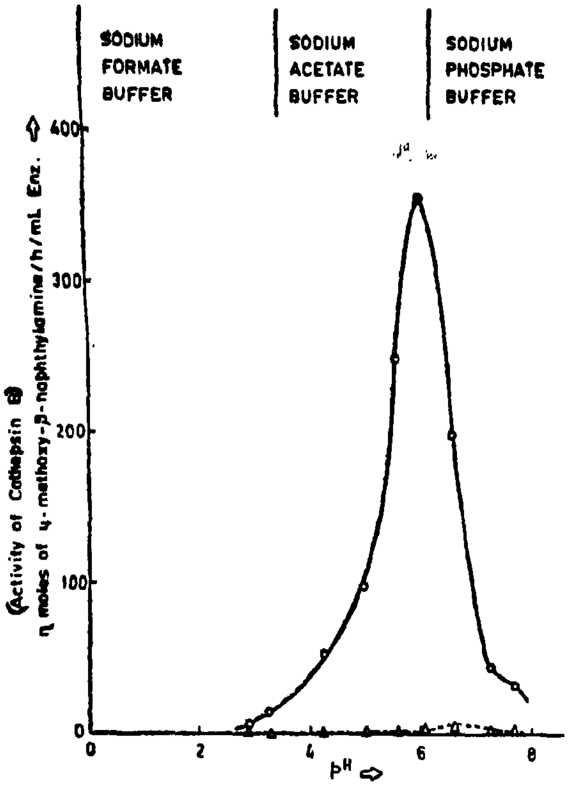


Fig. 8. Cathepsin B activity of rabbit brain tissue at various pH values, Z-Arg-Arg-4mβNA as substrate. Enzyme activity expressed as nanomole of 4-methoxy-β-naphthylamine liberated/h/ml enzyme at 40°; activity without leupeptin (O), and activity with leupeptin (▽).

laboratory to identify cathepsin L in brain and also to analyse the proteases present in peak III.

The following conclusion can be interpreted from the experiments carried out on brain tissue with regard to its protease activity. The brain tissue contains proteases active over the entire pH range from pH 2.0 to 10.0. The protease peak at slightly acidic pH values which tends to be masked when traditional substrate Hb and casein are utilised, can be made apparent by using a chromogenic substrate, azocasein. This second peak in the activity profile consists of cathepsin B and a BANA-hydrolase, has been proved by using a specific inhibitor and a specific substrate of cathepsin B, namely leupeptin and Z-Arg-Arg-4mβNA, respectively. The presence of cathepsin L has not yet been reported from brain tissue. The work in this direction is in progress in addition to the work for identification of the third protease peak at alkaline pH values.

Acknowledgement

The authors thank Prof. George Kalnitsky and Drs. Ranjit Chatterjee and Vijay K. Chadha, Department of Biochemistry, University of Iowa, Iowa City, Iowa (U.S.A.) for the generous gifts of substrates and inhibitors. Thanks are due to Prof. H. K. Pujari for his keen interest and Dr. V. Srinivasan for allowing us use of uv/visible Shimadzu-140 spectrophotometer. Two of the authors (M.L. and K.M.) thank C.S.I.R., New Delhi for providing Junior Research Fellowships.

References

1. N. MARKS in "Peptides in Neurobiology", ed. H. GAINER, Plenum Press, New York, 1977, p. 221.
2. S. S. OJA and A. A. HEINAEMAEKI, *Chem. Abstr.*, 1981, **94**, 12082.
3. J. N. WHITAKER, *J. Neurochem.*, 1980, **34**, 284.
4. N. MARKS, M. BENUCK and G. A. HASHIM, *J. Neurosci. Res.*, 1980, **5**, 217.
5. M. ORLOWSKI, E. WILK, S. PEARSE and S. WILK, *J. Neurochem.*, 1979, 33, 461 ; S. WILK and M. ORLOWSKI, *J. Neurochem.*, 1980, **35**, 1172.
6. L. B. HERSH and J. F. MCKLEVY, *J. Neurochem.*, 1981, **36**, 171.
7. A. KAUR and H. SINGH, *Curr. Sci.*, 1982, **51**, 926.
8. H. KIRSCHKE, J. LANGNER, B. WIEDERANDERS, S. ANSORGE, P. BOHLEY and H. HANSON, *Acta Biol. Med. Germ*, 1976, 35, 285.
9. A. J. BARRETT in "Proteinases in Mamallian Cells and Tissues", ed. A. J. BARRETT, North Holland Publishing Co., Amsterdam, 1977, p. 181.
10. O. H. LOWRY, N. J. ROSEBROUGH, A. L. FARR and R. J. RANDALL, *J. Biol. Chem.*, 1951, **193**, 265.
11. H. SINGH and G. KALNITSKY, *J. Biol. Chem.*, 1978, **253**, 4319.
12. H. SINGH and G. KALNITSKY, *J. Biol. Chem.*, 1980, **255**, 369.
13. H. SINGH, K. TSUNGMIN and G. KALNITSKY in "Protein Turnover and Lysosome Function", eds. H. SEGAL and D. J. DOYLE, Academic Press, New York, 1978, p. 315.
14. N. MARKS and A. SUHAR, *Eur. J. Biochem.*, 1979, **101**, 23.
15. J. K. MCDONALD and S. ELLIS, *Life Sci.*, 1975, **17**, 1269.

pp. 1061-1064

Fungicidal Activities and Mass Spectral Studies of Some Schiff Bases Derived from *para*-Hydroxybenzaldehyde and Their Derivatives

B. DASH*, P. K. MAHAPATRA, D. PANDA and (MRS.) J. M. PATTNAIK

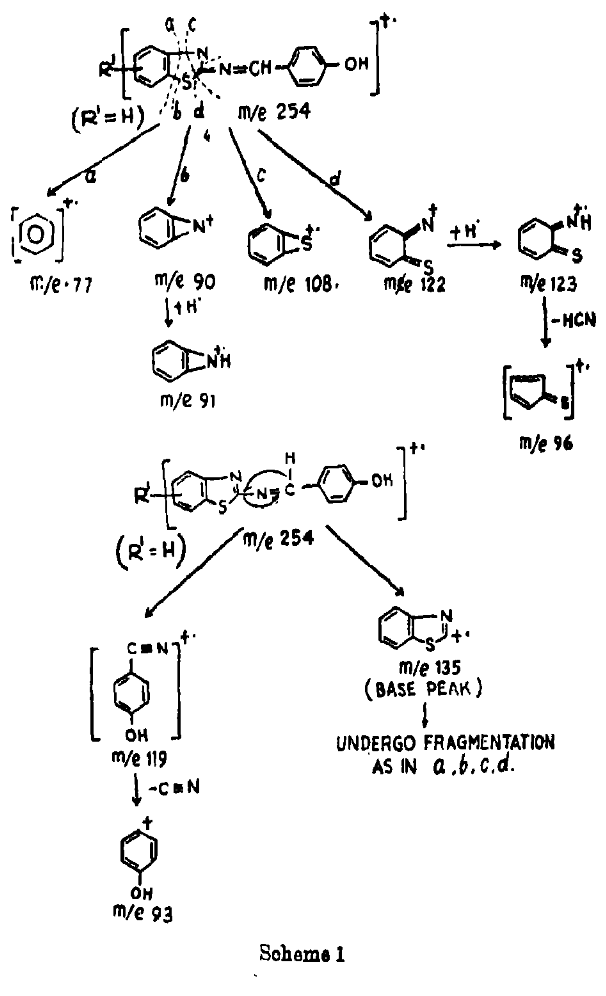
Department of Chemistry, Utkal University, Bhubaneswar-751 004

A new series of Schiff bases derived from 4-substituted, 4,5-disubstituted-2-aminothiazoles, substituted-2-aminobenzothiazoles and p-hydroxybenzaldehyde was synthesised. Condensation of the Schiff bases with chloroacetylchloride and subsequent reaction with piperidine and morpholine yielded corresponding acetoxy derivatives. Cycloaddition of the Schiff bases with thioglycollic acid yielded thiazolidinone derivatives. The compounds were characterised by elemental analysis, ir and mass spectra and screened for their fungicidal activity.

IT has been observed that the biological activity of certain organic compounds is related to their ability for complex formation with metal ions[1]. Many of the anticancer drugs are also viable ligands[2]. The importance of thiazole and benzothiazole derivatives, and Schiff bases as biologically active compounds are well known. Schiff base complexes have been suggested as models for enzymes such as galactose oxidase[3]. All these observations and the essential role of azomethin linkage in certain biological reactions prompted us to synthesise some Schiff bases having thiazole nucleus. These Schiff bases, prepared by the condensation of 2-aminothiazoles and 2-aminobenzothiazoles with salicylaldehyde, 5-bromo and 3,5-dibromo salicylaldehydes were also found to be very good ligands[4,5]. In the present communication, we report the synthesis and fungicidal activity of some new thiazole and benzothiazole Schiff bases which differ considerably from the above Schiff bases as regards to their chelating ability.

The Schiff bases were prepared by condensation of the corresponding aldehydes with substituted 2-aminothiazoles and benzothiazoles. Condensation of these Schiff bases with chloroacetyl chloride yielded the corresponding chloroacetyl derivatives which on further reaction with morpholine and piperidine formed the corresponding morpholino and piperidino acetoxy compounds. Cycloaddition of the Schiff bases with thioglycollic acid gave the corresponding thiazolidinone derivatives.

The structure of the Schiff bases was elucidated on the basis of elemental analysis, ir and mass spectra. The ir spectra of Schiff bases showed a sharp band around 3450 cm^{-1} and a broad medium band around 3100 cm^{-1} (free and bonded - OH) and a strong sharp band in the region 1640-1625 cm^{-1} (C=N). On thiazolidinone formation, the band due to C=N stretching is lost and a strong tertiary amide stretch (N-C=O) is observed around 1680 cm^{-1}. Disappearance of the OH band

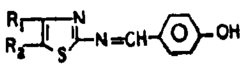


Scheme 1

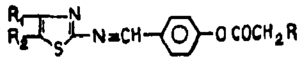
and appearance of a new band around 1715-1725 cm^{-1} established the formation of acetoxy derivatives.

The main mass spectral fragmentation pattern of the Schiff bases derived from 4-aryl- and 4,5-diaryl-

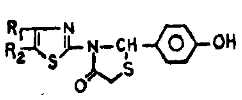
thiazoles is similar to that of the Schiff bases reported earlier[4]. All of them give stable molecular ions (base peak in most cases) and $(M-1)^+$ peaks. Other characteristic fragments observed were formed by the loss of CO, SH and HCN radicals. The (M – CH =S) and (M – OH) peaks observed in earlier Schiff bases are not observed in the present series. The mass spectral fragmentation pattern of one representative member of the series of Schiff bases derived from 2-aminobenzothiazoles (4, R = H) is depicted in Scheme 1. Surprisingly, the percentage of molecular ion peak and (M-1) peak is much low in comparison to other Schiff bases. The main fragmentation process involves rupture of 1,9 and 3,8, 1,9 and 2,3, 1,2 and 3,8, and 1,2 and 2,3 bonds of the benzothiazole nucleus [5-7]. Other characteristic fragments observed were due to the loss of CHO, CH_2O, $(CH_2O+C_2H_2)$ radicals from the molecular ion. Most of the fragmentation patterns were supported by the appearance of appropriate metastable peaks.



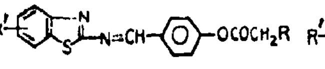
1



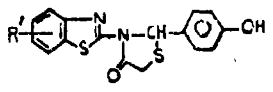
2



3



5



6

Experimental

Melting points were determined in open capillary tube and are uncorrected. Ir spectra were determined in Perkin-Elmer 337 grating infrared spectrophotometer in nujol mull. Mass spectra were recorded on a varian MAT SM 1-BH mass spectrophotometer at 70 ev at C.D.R.I., Lucknow.

4-Aryl-2-aminothiazoles were prepared by the condensation of substituted acetophenone with thiourea in presence of iodine[8] and 4,5-diaryl-2-aminothiazoles were prepared from their respective desyl chloride[9] and thiourea. Substituted 2-aminobenzothiazoles were prepared from the respective thioureas[10].

4',5'-Diphenylthiazole-2'-imino-(4-hydroxy)-benzylidene (1, $R_1=R_2=C_6H_5$) : A mixture of 2-amino-4,5-diphenylthiazole (0.01 mol), *p*-hydroxybenzaldehyde (0.01 mol) in ethanol (30 ml) and piperidine (3-4 drops) was refluxed for 1.5 h on a water bath. The reaction mixture was then cooled and the solid separated was filtered and crystallised from ethanol (75%), m.p. 201° (Found : C, 74.00 ; H, 4.20 ; N, 7.50. $C_{22}H_{16}N_2OS$ requires C, 74.15 ; H, 4.50 ; N, 7.86%). In a similar way, other substituted thiazole/benzothiazole-imino-(4-hydroxy)-benzylidenes were prepared. Melting point, yield and antifungal activity are given in Tables 1 and 2.

TABLE 1—SCHIFF BASES (1)*

Sl. no.	R_1	R_2	M.p. °C	% Inhibition on *Curvularia* at 500 ppm
1.	C_6H_5	H	110	81.5
2.	p-$CH_3.C_6H_4$	H	150	84.6
3.	p-$Cl.C_6H_4$	H	195	87.2
4.	p-$OCH_3.C_6H_4$	H	203	87.8
5.	p-$Br.C_6H_4$	H	221	88.1
6.	α-Naphthyl	H	238	89.1
7.	C_6H_5	C_6H_5	201	82.8
8.	p-$OCH_3.C_6H_4$	p-$OCH_3.C_6H_4$	150	87.8
9.	p-$Cl.C_6H_4$	p-$Cl.C_6H_4$	120	88.9

* Elemental analyses (C, H, N) within ±0.5% of theoretical values. Yields between 60-75%.

TABLE 2—SCHIFF BASES (4)*

Sl. no.	R'	M.p. °C	% Inhibition on *Curvularia* at 500 ppm
1.	H	185	80.5
2.	6-Cl	188	85.4
3.	6-CH_3	240	82.3
4.	6-OCH_3	198	84.7
5.	4-CH_3	160	81.6

* Elemental analyses (C, H, N) within ±0.5% of theoretical values. Yields between 55-70%.

4',5'-Diphenylthiazole-2'-imino-(4-chloroacetoxy)-benzylidene (2, R – Cl, $R_1=R_2=C_6H_5$) : A mixture of 1 (0.01 mol), chloroacetyl chloride (0.015 mol) in dry benzene (15-20 ml) and pyridine (2-3 drops) was refluxed for 5 h on water bath. After reflux, the excess of benzene and pyridine were removed under reduced pressure. The residue obtained was washed thoroughly with water and crystallised from ethanol (65%), m.p. 115° (Found : N, 5.15 ; Cl, 7.59. $C_{24}H_{17}O_2SCl$ requires N, 5.39 ; Cl, 7.86%). Other substituted thiazole/benzothiazole-imino-(4-chloroacetoxy)-benzylidenes were prepared similarly.

4',5'-Diphenylthiazole-2'-imino-(4-morpholinoacetoxy)-benzylidene (2, R = morpholinyl, $R_1=R_2=C_6H_5$) : A mixture of 4',5'-diphenylthiazole-2'-imino-(4-chloroacetoxy)-benzylidene (2, R = Cl, $R_1=R_2=C_6H_5$)(0.005 mol) and morpholine (0.01 mol) in dry benzene (25 ml) was refluxed for 8 h on water bath. After reflux, excess of benzene was removed under reduced pressure. The solid mass, then obtained was filtered, dried and crystallised from ethanol (60%), m.p. 188° (Found : C, 66.6 ; H, 4.80 ; N, 8.55, $C_{28}H_{25}N_3O_3S$ requires C, 70.15 ; H, 4.60 ; N, 8.77%). In a similar way, other substituted thiazole/benzothiazole-imino-(4-morpholino/piperidino acetoxy)benzylidenes were prepared.

Melting point, yield and antifungal activity are given in Tables 3 and 4.

TABLE 3—ACETOXY SCHIFF BASES (2)*

Sl. no.	R_1	R_2	M.p. °C	% Inhibition in *Curvularia* at 500 ppm
	R=morpholinyl			
1.	C_6H_5	H	105	69.5
2.	p-CH_3.C_6H_4	H	118	71.8
3.	p-Cl.C_6H_4	H	160	75.4
4.	p-OCH_3.C_6H_4	H	180	76.5
5.	p-Br.C_6H_4	H	185	74.2
6.	α-Naphthyl	H	215	79.8
7.	C_6H_5	C_6H_5	188	72.5
8.	p-OCH_3.C_6H_4	p-OCH_3.C_6H_4	121	74.9
9.	p-Cl.C_6H_4	p-Cl.C_6H_4	110	76.9
	R=Piperidine			
10.	C_6H_5	H	103	69.8
11.	p-CH_3.C_6H_4	H	106	72.0
12.	p-Cl.C_6H_4	H	152	75.6
13.	p-OCH_3.C_6H_4	H	125	76.8
14.	p-Br.C_6H_4	H	162	74.5
15.	α-Naphthyl	H	200	80.1
16.	C_6H_5	C_6H_5	115	72.8
17.	p-OCH_3.C_6H_4	p-OCH_3.C_6H_4	95	74.9
18.	p-Cl.C_6H_4	p-Cl.C_6H_4	105	76.9

* Elemental analyses (C, H, N) within ±0.5% of theoretical values. Yields between 50-65%.

TABLE 4—ACETOXY SCHIFF BASES (5)*

Sl. no.	R'	M.p. °C	% Inhibition on *Curvularia* at 500 ppm
	R=morpholinyl		
1.	H	187	70.4
2.	6-Cl	152	75.1
3.	6-CH_3	110	71.5
4.	6-OCH_3	198	74.6
5.	4-CH_3	170	72.1
	R=Piperidine		
6.	H	115	70.6
7.	6-Cl	105	75.4
8.	6-CH_3	95	72.3
9.	6-OCH_3	125	74.9
10.	4-CH_3	140	72.5

* Elemental analyses (C, H, N) within ±0.5% of theoretical values. Yields between 50-60%.

2-(4'-Hydroxyphenyl)-3-(4", 5"-diphenyl-thiazol-2"-yl)-4-thiazolidinone (**3**, $R_1=R_2=C_6H_5$) : A mixture of 4',5'-diphenylthiazole-2'-imino-(4-hydroxy)-benzylidene (**1**, $R_1=R_2=C_6H_5$) (0.01 mol), thioglycollic acid (0.015 mol) in dry benzene (30 ml) was refluxed for 6 h on water bath. After reflux, the reaction mixture was cooled and excess of benzene was removed under reduced pressure. The solid, thus obtained, was washed several times with $NaHCO_3$ solution and water and finally crystallised from ethanol (65%), m.p. 161° (Found: C, 55.50; H, 4.66; N, 6.12. $C_{24}H_{18}N_2O_2S_2$ requires C, 66.67; H, 4.17; N, 6.48%). In a similar way, other thiazolidones of the series were prepared. Melting point, yield and antifungal activity are given in Tables 5 and 6.

TABLE 5—THIAZOLIDINONES (3)*

Sl. no.	R_1	R_2	M.p. °C	% Inhibition on *Curvularia* at 500 ppm
1.	C_6H_5	H	160	56.1
2.	p-CH_3.C_6H_4	H	184	56.2
3.	p-Cl.C_6H_4	H	155	61.5
4.	p-OCH_3.C_6H_4	H	165	61.8
5.	p-Br.C_6H_4	H	190	59.5
6.	α-Naphthyl	H	>250	62.8
7.	C_6H_5	C_6H_5	161	57.2
8.	p-OCH_3.C_6H_4	p-OCH_3.C_6H_4	139	59.5
9.	p-Cl.C_6H_4	p-Cl.C_6H_4	112	61.5

* Elemental analyses (C, H, N) within ±0.5% of theoretical values. Yields between 55-60%.

TABLE 6—THIAZOLIDINONES (6)*

Sl. no.	R'	M.p. °C	% Inhibition on *Curvularia* at 500 ppm
1.	H	170	55.8
2.	6-Cl	184	62.7
3.	6-CH_3	218	59.4
4.	6-OCH_3	198	60.5
5.	6-CH_3	210	59.6

* Elemental analyses (C, H, N) within ±0.5% of theoretical values. Yields between 50-55%.

Fungicidal activity: For fungicidal assay poisoned food technique was used[11]. All the compounds were tested for their toxicity towards *Curvularia* species at a concentration of 500 ppm. The experiments were performed in duplicate and the average inhibition is reported. The percentage inhibition was calculated by the following expression.

$$\% \text{ Inhibition} = (1 - X/Y) \times 100$$

where X = weight of the growth of colony in test sample, and Y = weight of the growth of colony in the control sample.

The percentage inhibition of the germination of conidi of the above test fungus during 48 h is given in Tables 1-6. A few generalisation regarding the structure-activity relationship has been made. Among the compounds screened, the Schiff bases were the most active. But they are less active than the corresponding Schiff bases derived from 4-aryl-2-aminothiazoles and salicylaldehyde/5-bromo and 3,5-dibromosalicyladehyde[4]. The presence of halogen, naphthyl and methoxy groups in the compound enhances the fungicidal activity. It is also observed that the Schiff bases are more active than the corresponding thiazolidinones and acetoxy derivatives.

References

1. G. CONTRERAS and H. CORTES, *Inorg. Nucl. Chem. Lett.* 1970, **7**, 639.

2. D. R. WILLIAMS, *Chem. Rev.*, 1972, **72**, 203.

3. R. S. GIORDANO and R. D. BENEMAN, *J. Am. Chem. Soc.*, 1974, **96**, 1017, 1028.
4. B. DASH, M. PATRA and S. PRAHARAJ, *Indian J. Chem.*, *Sect. B*, 1980, **19**, 894.
5. B. DASH and S. K. MAHAPATRA, *J. Inorg. Nucl. Chem.*, 1975, **37**, 271.
6. H. OGURA and S. SUGIMOTO, *Org. Mass Spectrom.*, 1970, **3**, 1341.
7. Q. N. PORTER and J. BALDAS, "Mass Spectrometry of Heterocyclic Compounds", John Wiley, 1970, p. 582.
8. B. DASH and M. K. ROUT, *J. Indian Chem. Soc.*, 1955, **32**, 807.
9. L. F. FIESER, "Experiments in Organic Chemistry", 3rd. Ed., D. C. Health and Company, Boston, 1957, p. 180.
10. P. N. BHARGAVA and B. T. BALIGA, *J. Indian Chem. Soc.*, 1958, **38**, 807.
11. Y. L. NENE, "Fungicidal Plant Disease Control", Oxford and I. B. H., New Delhi, 1971.

J. Indian Chem. Soc.,
Vol. LXI, November, Decemeer 1984, pp. 1065-1068

Kinetic and Mechanistic Study of Nitrite by Bromate and Ruthenium(III) Catalysed Iodate

P. S. RADHAKRISHNAMURTI*, B. K. PANDA and G. K. MOHANTY

Department of Chemistry, Berhampur University, Berhampur-760 007

Kinetic studies of the oxidation of nitrite by bromate at $pH \approx 3$ and Ru^{III} catalysed iodate at 0.01 *M* $[HClO_4]$ have been studied. The reactions are acid catalysed. Ionic strength effects and effect of added salts are found to be marginal. The rate laws for the bromate oxidation and Ru^{III} catalysed iodate reaction have been discussed.

THE present study is concerned with the oxidation of nitrite by bromate and Ru^{II} catalysed iodate. As there is no perceptible reaction with iodate under the experimental conditions employed, a transition metal ion Ru^{III} has been chosen as a catalyst. Interestingly the reaction is facile in the presence of Ru^{III}. Hence, a detailed kinetic study is attempted.

Experimental

All the reagents used were of AnalaR (B.D.H.) grade, 70% BDH (AR) $HClO_4$, $RuCl_3$ (Johnson and Mathey) was standardised by the method of Horiuchi *et al.*[1] and the desired concentration was maintained by dilution. Sodium nitrite (E. Merck) solutions were standardised cerimetrically[2]. The kinetics of the reaction was followed by estimating the unreacted bromate or iodate idometrically towards conventional starch end point. In all the kinetic runs 5 ml aliquots were added to 50 ml ice-cold water containing sulphamic acid. Sulphamic acid decomposed nitrite, which otherwise interferes with the iodometric determinations[3].

Potassium hydrogen phthalate and hydrochloric acid were used to maintain the *p*H which was measured by using a Systronic 335 Digital *p*H meter. The rate constants are reproducible within ±3% error.

Results and Discussion

Effect of varying $[BrO_3^-]$ *on the reaction rate :* The order with respect to bromate is unity (as evidenced from the linearity of log titre *vs* time plots up to at least three half lives). Moreover, the pseudo-first order rate constants computed from the slopes of these plots are almost constant over a six fold variation in the initial concentration of bromate (Table 1).

Effect of varying $[IO_3^-]$ *on the reaction rate :* The order with respect to oxidant is proved to be zero as the plots of percentage *vs* time are fairly linear up to at least two half lives. Zero order rate constants are computed from slopes (x/t) of such linear plots. Moreover, k_0 values computed for various initial concentration of IO_3^- are almost identical, confirming the zero order dependence with respect to the oxidant (Table 2) in the concentration range studied. Such zero order dependence has been observed in various reactions catalysed by transition metal ions.

TABLE 1—EFFECT OF VARYING $[BrO_3^-]$, $[NaClO_4]$, $[NO_3^-]$ AND $[Cl^-]$ ON THE RATE

$[NO_2^-] = 0.005$ *M* pH = 2.9 Temp. = 35°

$[BrO_3^-]$ $\times 10^4$ *M*	$[NaClO_4]$ $\times 10^3$ *M*	$[NO_3^-]$ $\times 10^3$ *M*	$[Cl^-]$ $\times 10^3$ *M*	k_1 $\times 10^2$ min^{-1}
2.5	5.0	—	—	1.84
5.0	—	—	—	1.92
8.8	—	—	—	1.88
14.8	—	—	—	1.85
5.0	10.0	—	—	1.92
—	15.0	—	—	1.95
5.0	5.0	5.0	—	2.08
—	—	10.0	—	2.09
5.0	5.0	—	1.0	1.77

Effect of varying $[NO_2^-]$ *on the reaction rate :* The rate of the reaction increases on increasing $[NO_2^-]$ (Table 3). The plot of log k_1 *vs* log $[NO_2^-]$ is a straight line at a fixed *p*H 3 for bromate oxidation. For iodate oxidation this slope is found to be unity.

Effect of added salts and ionic strength on the rate : The bromate oxidation reaction has been followed in the presence of salts like, KCl, $NaNO_3$ and $NaClO_4$. The salts are found to have almost no influence on the rate. The iodate oxidation has been studied at various concentrations of $NaClO_4$ and no change in rate has been observed (Table 1).

Effect of varying solvent mixture on the rate : Results in Table 4 reveal that the bromate oxidation rate increases on decreasing the dielectric constant of the medium, whereas the iodate oxidation rate (Table 5) is insensitive to the changes in dielectric constant.

Effect of changing pH *on the ratio :* The bromate oxidation reaction is immeasurably fast below *p*H 2

Table 2—Effect of Variation of [Oxidant], [Substrate], [Acid], [Catalyst] and [$NaClO_4$] at Temperature 35°

Substrate [NO_2^-] $\times 10^3$ M	Oxidant [IO_3^-] $\times 10^4$ M	Acid [$HClO_4$] $\times 10^2$ M	Catalyst [Ru^{III}] $\times 10^6$ M	[$NaClO_4$] $\times 10^2$ M	K_0 $\times 10^{-2}$ mol l^{-1} min^{-1}
5.0	2.6	1.0	1.528	5.0	1.43
5.0	5.2	1.0	1.528	5.0	1.40
5.0	11.3	1.0	1.528	5.0	1.48
5.0	20.9	1.0	1.528	5.0	1.38
2.5	5.0	1.0	1.528	5.0	0.91
10.0	5.0	1.0	1.528	5.0	3.2
20.0	5.0	1.0	1.528	5.0	5.6
5.0	5.0	1.0	0.382	5.0	0.35
5.0	5.0	1.0	0.764	5.0	0.73
5.0	5.0	1.0	3.056	5.0	2.86
5.0	5.0	0.5	1.528	5.0	0.79
5.0	5.0	2.0	1.528	5.0	2.54
5.0	5.0	4.0	1.528	5.0	3.94
5.0	5.0	1.0	1.528	2.5	1.57
5.0	5.0	1.0	1.828	10.0	1.6
5.0	5.0	1.0	1.528	15.0	1.6

Table 3—Effect of Variation of [NO_2^-] on the Reaction Rate

[BrO_3^-]=5×10^{-4} M, Aqueous medium; [$NaClO_4$]=0.05 M; Temp.=35°, pH=3

[NO_2^-] $\times 10^3$ M	k_1 $\times 10^3$ min^{-1}
2.8	0.70
5.0	1.23
10.0	2.30
15.0	3.84

Table 4—Effect of Different Solvents on the Rate

[NO_2^-]=0.005 M, [$NaClO_4$]=0.05 M, [BrO_3^-]=0.0005 M, Temp.=35°

Solvent	% (v/v)	pH	k_1 $\times 10^3$ min^{-1}
Dimethyl sulphoxide	20	3.53	0.96
Acetonitrile	20	3.30	1.09
Acetic acid and 0.1 M sodium acetate	25	2.68	6.40
Acetic acid and 0.02 M sodium acetate	15	2.36	10.36

Table 5—Effect of Variation of Percentage of HOAc, on the Reaction Rate

[IO_3^-]=0.0005 M, [NO_2^-]=0.005 M, [$HClO_4$]=0.01 M, [Ru^{III}]=1.528×10^{-6} M, [$NaClO_4$]=0.05 M, Temp.=35°

HOAc %	k_0 $\times 10^{-2}$ mol l^{-1} min^{-1}
0	1.42
5	1.52
10	1.48
20	1.62
40	1.65

and imperceptibly slow beyond pH 4. For all kinetic runs, therefore, the pH of the solution was varied around 3 by keeping the concentration of potassium hydrogen phthalate constant and changing the concentration of hydrochloric acid in the buffer in the reaction mixture (Table 6). At this pH the decomposition of nitrite is minimum and almost negligible. The log k values are found to vary linearly with pH. Increase in the concentration of $HClO_4$ increases the rate of iodate oxidation (Table 2). The plot of log k_0 *vs* log [H^+] is linear with positive slope of less than unity indicating fractional dependence on acid.

Table 6—Effect of Changing pH on the Rate

[BrO_3^-]=5×10^{-4} M, Aqueous medium, [$NaClO_4$]=0.05 M, [NO_2^-]=5×10^{-3} M, Temp.=35°

pH	k_1 $\times 10^3$ min^{-1}
2.43	6.40
2.55	4.10
2.87	1.92
3.0	1.23
3.05	1.15
3.30	0.58
3.55	0.25
3.74	0.18

Effect of varying temperature on the rate : The reactions are carried out at different temperatures (35, 40, 45 and 50°) with a view to compute the Arrhenius activation parameters. The plot of log (rate constant) *vs* 1/T is found to be linear. The values of $\Delta E^{\neq}$, $\Delta H^{\neq}$, $\log_{10}A$ and $\Delta S^{\neq}$ are 67.0 kJ mol^{-1}, 64.4 kJ mol^{-1}, 7.8 and -103.0 J mol^{-1} K^{-1}, respectively for bromate oxidation and 35.9 kJ mol^{-1}, 33.3 kJ mol^{-1}, 0.76 and -239.1 J mol^{-1} K^{-1}, respectively for iodate oxidation.

Effect of varying [Ru^{III}] on the iodate oxidation reaction rate : The oxidation potential of BrO_3^- is 1.44 V and that of IO_3^- is 1.08 V. The low potential of iodate system is probably the reason why it is ineffective to oxidise HNO_2. However, in presence of catalytic amount of a transition metal ion, Ru^{III}, the reaction becomes facile. Increasing the concentration of Ru^{III} increases the reaction rate (Table 2). The plot of log k_0 *vs* log [Ru^{III}] is

linear with unit slope indicating first order dependence with respect to $[Ru^{III}]$.

Nature of nitrite species : Nitrite ion in acid solution exists in a number of forms[4], *viz.* NO^+, $H_2NO_2^+$, N_2O_3, HNO_2 and NO_2^- itself. It has been reported[5] that no trace of N_2O_3 is found in dilute solutions of nitrous acid (10^{-3} *M*). Again, the participation of nitrosonium ion is highly unlikely under mild acid conditions ($pH \approx 2$)[6]. The nitrosonium ion or its hydrated form (H_2NO_2) is present only in very highly acidic solutions[7]. At low concentration of nitrite (<0.05 *M*) and acidity (<0.2 *M*), undissociated nitrous acid and NO_2^+ are the only species present in appreciable concentrations[8]. Under the present experimental conditions of low $[NO_2^-]$ and low acidity the undissociated HNO_2 and NO_2^- are the only species present.

Nature of bromate species : Edwards[9] in his studies of exchange of water with bromate has postulated the following equilibria.

$$H^+ + BrO_3^- \rightleftharpoons HBrO_3 \quad \text{(fast)}$$
$$H^+ + HBrO_3 \rightleftharpoons H_2BrO_3^+ \quad \text{(fast)}$$

However, the possibility of H_2BrO_3 is reasonable at and above 0.1 *M* acidity. This also receives support from Birk[10].

Under our experimental condition of low acidity the existence of the species $H_2BrO_3^+$ is highly unlikely. Hence, the probable species that takes part in the oxidation reaction are BrO_3^- and $HBrO_3$, the latter being less favourable than the former.

Mechanism of bromate oxidation : The following results emerge from a detailed kinetic study of the oxidation of nitrite by bromate.

(i) First order each in bromate and NO_2^-.
(ii) Order with respect to acidity is more than one.
(iii) Ionic strength effect and salt effect is marginal.
(iv) Decrease in dielectric constant of the medium accelerates the reaction.

Of the two nitrite species, *i.e.* undissociated nitrous acid and free nitrite, the former is taken as the active species that takes part in the reduction process in line with many earlier work. In the present investigation as $[NO_2^-]$ is maintained more than $[BrO_3^-]$ in all the runs and as the two reactants have a tendency to undergo two electron transfer, the sequence $BrO_3^- \rightarrow BrO_2^- \rightarrow BrO^- \rightarrow Br^-$ is more likely. This finds support from the stoichiometry of 3 : 1 ($[NO_2^-]$: $[BrO_3^-]$) by keeping excess of [bromate] over $[NO_2^-]$. A stoichiometry of 3 : 1 ([Hg] : $[BrO_3^-]$) has also been observed earlier[11] in the oxidation of Hg° by bromate, where six electron reduction of bromate to bromide has been reported ($BrO_3^- \rightarrow BrO_2^- \rightarrow BrO^- \rightarrow Br^-$), the first stage of two electron change being rate determining followed by subsequent fast steps. In view of the above the following reactions is likely.

$$3HNO_2 + BrO_3^- = 3HNO_3 + Br^-.$$

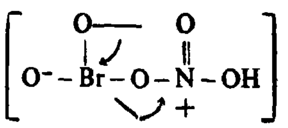
Under the experimental condition of excess $[NO_2^-]$ over [bromate], the final products are HNO_3 and Br^- since no bromate would be left to react with Br^- to complicate the reaction.

Hence, a nucleophilic attack of nitrogen lone pair on the bromate oxygen takes place in a slow step to form an intermediate complex which breaks down in a fast step to form NO_3^- and BrO_2^-. The BrO_2^- thus formed is reduced in two steps by NO_2^- to Br^- finally. In addition to this a parallel reaction between HNO_2 and $HBrO_3$ (though in small concentration) is also proposed in view of the complex dependence on acidity. A high negative entropy value also is in support of a rigid transition state complex.

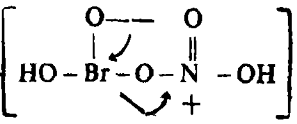
Thus the following scheme is proposed,

$$NO_2^- + H^+ \overset{K_a}{\rightleftharpoons} HNO_2$$

$$BrO_3^- + H^+ \overset{K_b \ll 1}{\rightleftharpoons} HBrO_3$$

$$BrO_3^- + HNO_2 \xrightarrow{k_1}$$ 

$$\longrightarrow BrO_2^- + NO_3^- + H^+$$

$$HBrO_3 + HNO_2 \xrightarrow{k_2}$$ 

$$\longrightarrow BrO_2^- + NO_3^- + 2H^+$$

$$HNO_2 + BrO_2^- \xrightarrow{fast} HNO_3 + BrO^-$$

$$HNO_2 + BrO^- \xrightarrow{fast} HNO_3 + Br^-$$

The dependence on acidity as evidenced from the plot of log k_1 *vs* log $[H^+]$ with slope of 1.2 prompts us to believe that a parallel reaction involving $HBrO_3$ and HNO_2 is also taking place though of less significance which explains the overall complex acidity dependence.

The rate equation basing on the mechanism can be expressed by equation (1), under the aprroximation $K_b \ll 1$ and $K_a[H^+] \ll 1$.

$$\text{Rate} = V$$
$$= K_a[H^+][NO_2^-]_T\{k_1[Br(V)]_T + k_2K_b[Br(V)]_T[H^+]\} \quad (1)$$

A plot of observed rate *vs* $[H^+]$ is not linear but slightly curved, as such the contribution from the second term, though small, is more pronounced at higher acidities. At lower acidities the second term containing $[H^+]^2$ will be too small to be of any significance. Hence, as the acidity increases a gradual upward bend is observed in the plot of k_1 *vs* $[H^+]$.

Dividing equation (1) throughout by $[H^+]^2$, we get,

$$\frac{\text{Observed rate}}{[H^+]^2}=K_a[NO_2^-]_T\left\{\frac{k_1}{[H^+]}+k_a k_b\right\} \qquad (2)$$

Equation (2) requires that a plot of observed rate/ $/[H^+]^2$ *vs* $1/[H^+]$ should be a straight line with an intercept on the rate axis which is in fact observed. This provides support in favour of the mechanism proposed and rate law derived. The small intercept obtained in the above plot is indicative of a very small contribution from the second term involving $HBrO_2$ in the absence of which a plot passing through the origin would have been obtained.

Mechanism of iodate reaction : It is well known that the transition metal ion easily form complexes due to the presence of vacant 'd' orbitals. In view of the fact that iodate in the present experiment does not participate in or prior to the rate determining step, complexation between Ru^{III} and HNO_2 in an equilibrium step is proposed. A very high negative entropy value is in agreement with the formation of an ordered transition state. The complex then breaks down in a slow step with an internal electron transfer to form Ru^{II}. The existence of Ru^{II} complexes are well known[12,13]. A rapid isomerisation of the nitro group from O-bound nitrito Ru^{III}-ONO to N-bound Ru^{III}-NO_2 takes place after which electron transfer occurs. A two electron oxidation of the nitro to nitrate occurs and the reduction is delocalised over two sites, *i.e.* metal and nitro group[14].

$$NO_2^- + H^+ \overset{K_a}{\rightleftharpoons} HNO_2$$

$$HNO_2 + Ru^{III} \overset{k_2}{\rightleftharpoons} \underset{\text{complex}}{[Ru^{III}\ldots HNO_2]}$$

$$\underset{\text{(complex)}}{[Ru^{III}\quad HNO_2]} \xrightarrow[\text{slow}]{k_3} Ru^{II} + NO_2^{\cdot} + H^+$$

$$Ru^{II} + NO_2^{\cdot} + IO_3^- \xrightarrow{\text{fast}} Ru^{III} + NO_3^- + IO_3^-$$

In view of the stability of various Ru^{II} complexes the above scheme is valid. The Ru^{II} thus formed is oxidised back to Ru^{III} in a fast step. $NO_2^{\cdot}$ radical as reaction intermediate has been reported[15] earlier in the nitrous acid oxidation by Mn^{III}.

Rate law : Applying steady state treatment for the formation and decomposition of the complex a rate expression (equation 3) can be written based on this mechanism.

$$V=\frac{k_2 k_3 K_a[NO_2^-]_T[H^+][Ru^{III}]}{(1+K_a[H^+])(k_{-2}+k_3)} \qquad (3)$$

This rate law explains all the observed facts.

So, a plot of 1/rate *vs* $1/[H^+]$ should be a straight line with an intercept on the inverse rate axis which is in fact observed. This proves the validity of the mechanism and the corresponding rate law derived.

Acknowledgement

The authors thank to C.S.I.R. and U.G.C., New Delhi for financial assistance in way of fellowship to two of them (G.K.M. and B.K.P.).

References

1. Y. Horiuchi and O. Ichiyyo, *Chem. Abstr.*, 1970, 72, 50624.
2. H. H. Willard and P. Young, *J. Am. Chem. Soc.*, 1933, 55, 3260.
3. S. Kapoor and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, 1977, 39, 1019.
4. N. S. Bayliss and B. W. Watts, *Aust. J. Chem.*, 1956, 9, 319.
5. T. A. Turnky and C. A. Wright, *J. Chem. Soc.*, 1958, 2415.
6. G. Stedman, *J. Chem. Soc.*, 1959, 2948, 2949.
7. K. Jones, "The Chemistry of Nitrogen, Peragmon Texts in Inorganic Chemistry", Peragmon, Oxford, 1973, Vol. IIb, pp. 372-78.
8. C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 1959, 3466.
9. J. O. Edwards, *Chem. Rev.*, 1952, 50, 455.
10. J. P. Birk, *Inorg. Chem.*, 1978, 17, 504.
11. R. Davies, B. Kipling and A. G. Sykes, *J. Am. Chem. Soc.*, 1973, 95, 7250.
12. J. C. Bailar, M. J. Emeleus, R. Nyholm and A. F. T. Dickenson, "Comprehensive Inorganic Chemistry", Pergamon, London, 1973, Vol. III, p. 1198.
13. P. S. Radhakrishnamurti and N. C. Sahu, *Kinet. Katal.*, 1981, 22, 627.
14. F. R. Keene, D. J. Salmon, J. L. Walsh, H. D. Abruna and T. J. Meyer., *Inorg. Chem.*, 1980, 19, 1896.
15. R. C. Thompson, *J. Am. Chem. Soc.*, 1971, 93, 7315.

Journal of the Indian Chemical Society

Vol. 61, 1984

AUTHOR INDEX

"D"

"E"

"F"

"G"

"K"

"N"

"O"

"S"

SUBJECT INDEX

"B"

"C"

"D"

"E"

"H"

"I"

"M"

"N"

"Q"

"T"

* The Publisher regrets that due to oversight similar communication has been published in the April 1984 issue of the Journal (pp. 872-74).

"U"

"V"

Book Review

J. Indian Chem. Soc.,
Vol. LXI, November, December 1984.